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HANDBOOK OF PREPARATIVE INORGANIC CHEMISTRY

VOLUME 2 · SECOND EDITION

Edited by GEORG BRAUER

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Translation Editor's Preface

The English version of Volume II of Brauer's "Handbook" follows the path of the very well received translation of Volume I. Again, some of the material and particularly the bibliography has been corrected and brought up to date. The nomenclature has been revised where necessary, with the Stock and the Stock-Werner systems (the practice of using Roman numerals to define oxidation states of atoms) adopted as much as possible. This conforms with current I.U.P.A.C. and Chemical Abstracts practice [for details of this, see Robert C. Brasted, J. Chem. Education 35, 136 (1948)]. The references to laboratory equipment and techniques reflect current U.S. usage, but useful European methods have been retained.

It is hoped that this volume will be as well received as the preceding one. Comments from users are invited to help improve future editions.

Paul G. Stecher

Rahway, N. J.
May 1965

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SECTION 19

Copper, Silver, Gold

O. GLEMSER AND H. SAUER

Copper (Pure Metal)

$$\underset{79.5}{CuO} + \underset{22.4\,l.}{H_2} = \underset{63.5}{Cu} + \underset{18.0}{H_2O}$$

A solution of electrolytic copper in 30% nitric acid is evaporated to dryness. The resultant nitrate is converted to the oxide by heating for 15 hours in an electrical furnace at 850°C. The oxide is then reduced at low temperature (250–300°C). The product is finely divided metallic copper.

Alternate method: Reduction of copper oxalate with hydrogen [K. Fischbeck and O. Dorner, Z. anorg. allg. Chem. 182, 228 (1928)]. For preparative directions, see subsection on CuS, p. 1018.

DropBooks

PROPERTIES:

Atomic weight 63.54; m.p. 1084°C, b.p. 2595°C; $d_4^{20°}$ 8.93. Crystal structure: type A1.

REFERENCE:

H. Haraldsen, Z. anorg. allg. Chem. 240, 339 (1939).

Colloidal Copper

An ammoniacal solution of $CuSO_4$ (1:1000) is treated with a dilute solution of hydrazine hydrate (1:2000) in the presence of acacia (gum arabic). The hydrosol obtained upon heating is immediately poured into a parchment paper bag which has been presoaked in water for some time; it is dialyzed against water for four days.

PROPERTIES:

The hydrosol is copper-red under incident light and blue under transmitted light. If protected from air, it is stable for a limited time.

REFERENCE:

A. Guthier and G. Hofmeier. Z. anorg. allg. Chem. 44, 227 (1905).

Copper Hydride

CuH

I. $$4\,CuI + LiAlH_4 = LiI + AlI_3 + 4\,CuH$$
$$761.8 \quad 38.0 \quad 133.9 \quad 407.7 \quad 258.3$$

A pyridine solution of CuI is made to react at room temperature with a solution of $LiAlH_4$ in ether–pyridine (the latter being prepared by mixing a concentrated ether solution of $LiAlH_4$ with absolute pyridine), yielding a blood-red pyridine solution of CuH. The mixture is allowed to stand at room temperature for 4–6 hours to complete the reaction. The AlI_3 co-product is sparingly soluble in pyridine and precipitates to a large extent. It is then readily separated from the clear supernatant liquor by centrifugation. The residual AlI_3 and the soluble LiI are separated from the CuH by addition of an at least equal volume of ether to the pyridine solution. The resultant red-brown precipitate of CuH is separated by centrifugation, washed with ether, dissolved in pyridine, and reprecipitated with ether. This purification procedure is repeated twice. The ether is then evaporated in a high vacuum.

The reaction may also be carried out by treating a solution of CuI in pyridine–tetrahydrofuran–ether with an ether solution of lithium aluminum hydride. In this case, CuH precipitates as soon as the two solutions are mixed, while both AlI_3 and LiI remain in solution. The CuH precipitate is then purified as above (by dissolving in pyridine and reprecipitating with ether).

II. PREPARATION OF COPPER HYDRIDE BY REDUCTION OF SOLUTIONS OF COPPER SALTS WITH HYPOPHOSPHOROUS ACID

A 65°C mixture of 25 g. of $CuSO_4 \cdot 5\,H_2O$ in 100 ml. of water and 20 ml. of 2N H_2SO_4 is added to a solution of 21 g. of H_3PO_2 in 300 ml. of water. After standing for 24 hours, the resultant precipitate is filtered and washed successively with water, alcohol and ether. Although the precipitation is not quantitative under these conditions, the product is relatively pure.

Small amounts of iron salt or halogen ion impurity interfere with the precipitation.

PROPERTIES:

Formula weight 64.55. Light red-brown color. Anhydrous when obtained by method I. Undecomposed (metastable) up to about 60°C; decomposes into the elements above this temperature, and

rapidly at 100°C. Quite stable in 0°C water; just as in the thermal decomposition, dissociates into metallic copper and H_2 from 45°C on, rapidly at 65°C. Dark red pyridine solution. Crystal structure: type B4 (expanded Cu lattice). Heat of formation: 5.1 kcal./mole.

REFERENCES:

I. E. Wiberg and W. Henle. Z. Naturforsch. 7b, 250 (1952).
II. O. Neunhoeffer and F. Nerdel. J. prakt. Chem. 144, 63 (1935); G. F. Hüttig and F. Brodkorb. Z. anorg. allg. Chem. 153, 235, 242 (1926).

Copper (I) Chloride

CuCl

$$2\,CuSO_4 + 2\,NaCl + SO_2 + 2\,H_2O = 2\,CuCl + Na_2SO_4 + 2\,H_2SO_4$$
$$(5\,H_2O)$$

499.4	116.9	22.41.	36.0	198.0	142.1	196.2

Gaseous SO_2 is bubbled through an aequous solution of 50 g. of $CuSO_4 \cdot 5\ H_2O$ and 24 g. of NaCl at 60–70°C until CuCl ceases to precipitate. The product is suction-filtered and washed with sulfurous acid, then with glacial acetic acid until the latter becomes colorless. The moist product is placed in a shallow dish or on a large watch glass and heated on a water bath until the odor of acetic acid is no longer detectable. It is stored in a tightly closed container.

Alternate methods: a) Acetyl chloride is added in drops to a boiling solution of cupric acetate in glacial acetic acid containing at least 50% of acetic anhydride by volume. When the color changes to yellow, the addition is stopped and the mixture is refluxed for 15 minutes. The resultant white solid is suction-filtered, washed with acetic anhydride, and dried at 140–150°C (D. Hardt, private communication).

b) Cupric chloride is heated to 150–200°C in glycerol. The CuCl obtained is filtered, washed with alcohol, and dried in vacuum [B. K. Vaidya, Nature (London) 123, 414 (1928)].

c) Reduction of $CuCl_2 \cdot 2\ H_2O$ in a Na_2SO_3 solution (R. N. Keller and H. D. Wycoff in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York–London, 1946, p. 1).

d) A solution of crystalline $CuCl_2$ in hydrochloric acid is reduced over copper with exclusion of air (use a Bunsen valve; for a description of the valve, see Hackh's Chemical Dictionary, 3rd ed., the Blakiston Co., Phila.–Toronto, 1944). The product is poured into water [M. Denigés, Compt. Rend. Hebd. Séances Acad. Sci. 108, 567 (1889)].

e) A mixture consisting of 1 part of $CuSO_4 \cdot 5\ H_2O$, 2 parts of NaCl and 1 part of Cu turnings is heated (use a Bunsen valve) with

10 parts of H_2O until the color disappears completely. The mixture is poured into water, and CuCl crystallizes out [M. Denigés, Comptes Rendus Hebd. Séances Acad. Sci. 108, 567 (1889)].

f) Sublimation of commercially pure CuCl over copper in a stream of HCl and argon at 900°C [J. B. Wagner and C. Wagner, J. Chem. Physics 26, 1597 (1957)].

SYNONYM:

Cuprous chloride.

PROPERTIES:

Formula weight 99.00. White crystalline material, M.p. 432°C, b.p. 1490°C; d_4^{25} 4.14, d_4^{423} 3.677. Sparingly soluble in water (25°C): 1.53 g./100 g. (partial decomposition in water: $2CuCl = Cu + CuCl_2$). Forms a green basic chloride in air. Soluble in hot conc. hydrochloric acid, conc. alkali chloride solutions, conc. aqueous ammonia. Crystal structure: type B3. Conversion into high-temperature modification of type B4 at 410°C. Heat of formation (25°C): − 32.2 kcal./mole.

REFERENCE:

M. Rosenfeld. Ber. dtsch. chem. Ges. 12, 954 (1879).

Copper (I) Bromide

CuBr

$$2\,CuSO_4 + 2\,KBr + SO_2 + 2\,H_2O = 2\,CuBr + 2\,H_2SO_4 + K_2SO_4$$
$$(5\,H_2O)$$

499.4	238.0	22.4 l.	36.0	286.9	196.2	174.3

Stoichiometric quantities of pure $CuSO_4 \cdot 5\,H_2O$ and KBr are dissolved in boiled distilled water and the solution is filtered through hard filter paper. It is then heated to a moderate temperature and a fast stream of pure SO_2 is passed through, with stirring, for about two hours. The passage of gas is continued until the mixture has cooled completely; the CuBr precipitates in the form of fine yellowish-white crystals. The solid is filtered while carefully excluding all light, resuspended 5-7 times in boiled distilled water into which some SO_2 is bubbled, and filtered again. The product is finally washed with SO_2-containing alcohol, followed by SO_2-containing ether. The salt is dried for 3-4 days over H_2SO_4 and KOH in a hydrogen atmosphere, and then in vacuum.

Alternate methods: a) Acetyl bromide is added in drops to a boiling solution of cupric acetate in glacial acetic acid, containing at least 50% of acetic anhydride by volume, until the solution becomes light green and a pure white precipitate appears (D. Hardt, private communication).

b) Another starting material consists of the mixture used in the preparation of ethyl bromide from alcohol, Br_2 and red phosphorus. The mixture is filtered and an excess of $CuSO_4 \cdot 5\ H_2O$ is added to the clear solution. The dark green solution is brought to a boil; crystallization soon follows [D. B. Briggs, J. Chem. Soc. (London) 127, 496 (1925)].

c) Synthesis from the elements [J. B. Wagner and C. Wagner, J. Chem. Physics 26, 1597 (1957)].

SYNONYM:

Cuprous bromide.

PROPERTIES:

Formula weight 143.46. Colorless crystals. M.p. 498°C, b.p. 1345°C; d_4^{25} 4.72. Insoluble in H_2O; soluble in hydrogen halide solutions, nitric acid and aqueous ammonia. Heat of formation (25°C): — 24.9 kcal./mole.

CuBr exists in three modifications: γ-CuBr (type B3) below 391°C, β-CuBr (type B4) between 391 and 470°C, α-CuBr (cubic) above 470°C.

REFERENCE:

DropBooks

J. N. Frers. Ber. dtsch. chem. Ges. 61, 377 (1928).

Copper (I) Iodide

CuI

$$2\,CuSO_4 + 2\,KI + SO_2 + 2\,H_2O = 2\,CuI + 2\,H_2SO_4 + K_2SO_4$$
$$(5\,H_2O)$$

499.4	332.0	22.4 l.	36.0	380.0	196.2	174.3

The compound is obtained as a pure white solid by precipitation of a solution of $CuSO_4 \cdot 5\ H_2O$ with KI in the presence of a slight excess of sulfurous acid. The product is washed with water containing a small amount of SO_2, then (with exclusion of air) with pure alcohol, and finally with anhydrous ether. It is then filtered with suction and freed in vacuum of the last traces of ether. Residual strongly adhering traces of water are best removed in a high vacuum, first at 110°C and finally somewhat above 400°C. A better product is obtained if a small quantity of iodine is added to the material after it has been dried at 110°C. This iodine is entirely removed at 400°C.

Alternate methods: a) Analogous to the preparation of CuBr from the reaction mixture used in the synthesis of ethyl iodide. Crystalline CuI is obtained [D. B. Briggs, J. Chem. Soc. (London) 127, 496 (1925)].

b) Synthesis from the elements [J. B. Wagner and C. Wagner, J. Chem. Physics 26, 1597 (1957)].

SYNONYM:

Cuprous iodide.

PROPERTIES:

Formula weight 190.45. Pure white crystalline powder. M.p. 605°C, b.p. 1336°C; d_4^{25} 5.63. Quite stable in light and air, melts without decomposition in high vacuum and in a stream of oxygen-free N_2. The solidified melt is clear and colorless (impure materials yield dark melts). Insoluble in H_2O; soluble in acids and aqueous ammonia; soluble in alkali iodides. Heat of formation (25°C): −16.2 kcal./mole.

CuI exists in three modifications: γ-CuI (type B3) below 402°C, β-CuI between 402 and 440°C, and α-CuI (cubic) above 440°C.

REFERENCE:

C. Tubandt, E. Rindtorff and W. Jost, Z. anorg. allg. Chem. 165, 195 (1927).

Copper (II) Chloride

$CuCl_2$

I. DEHYDRATION OF THE HYDRATE IN A STREAM OF HCl

Pure $CuCl_2 \cdot 2\ H_2O$ is recrystallized from dilute hydrochloric acid to remove traces of basic salt, and is then heated to constant weight at 140–150°C in a stream of dry HCl. The $CuCl_2$ is stored in a desiccator over H_2SO_4 and NaOH until all remaining traces of adhering HCl have been absorbed by the NaOH.

II.

$$\underset{181.6}{Cu(CH_3COO)_2} + 2\,\underset{157.0}{CH_3COCl} = \underset{134.5}{CuCl_2} + 2\,\underset{204.2}{(CH_3CO)_2O}$$

A) CUPRIC ACETATE SOLUTION

Glacial acetic acid containing a small quantity of acetic anhydride is placed in the solvent flask of a Soxhlet extractor. The extraction section of the apparatus is filled with copper turnings, air is introduced, and the solvent is brought to a boil. The solution becomes saturated with copper acetate after 1–2 hours.

B) ANHYDROUS CUPRIC CHLORIDE

The solution prepared in the Soxhlet via (A) is allowed to cool to 35°C, decanted from the solid which crystallizes out, and precipitated at 40–50°C with the stoichiometric quantity of acetyl chloride. Calculation of the stoichiometric quantity may be based on the solubility of cupric acetate in glacial acetic acid: 20 g./liter at 35°C. The precipitate is washed with either hot glacial acetic acid or cold acetic anhydride, both of which may be removed by a final washing with anhydrous ether. The product is dried at 120°C.

Alternate methods: a) High-vacuum dehydration of $CuCl_2 \cdot 2H_2O$ at 100°C [W. Biltz, Z. anorg. allg. Chem. 148, 207 (1925)].

b) Refluxing of $CuCl_2 \cdot 2H_2O$ in $SOCl_2$. Removal of the excess $SOCl_2$ by distillation and evaporation of residual solvent in vacuum [H. Hecht, Z. anorg. allg. Chem. 254, 37 (1947)].

SYNONYM:

Cupric chloride.

PROPERTIES:

Formula weight 134.45. Yellow, deliquescent mass. M.p. 630°C, b.p. 655°C; d_4^{25} 3.387. Soluble in H_2O and alcohol. Solubility in ethyl alcohol (0°C) 31.9 g.; in methyl alcohol (15.5°C) 67.8 g./100 ml. Soluble in acetone, yielding a dark green solution, which becomes yellow at high dilution. Heat of formation (25°C): −49.2 kcal./mole.

DropBooks

REFERENCES:

I. H. C. Jones and W. R. Veazey. Z. phys. Chem. 61, 654 (1908).
II. D. Hardt. Z. anorg. allg. Chem. (in press); private communication.

Copper (II) Bromide

$CuBr_2$

I. $$\underset{79.5}{CuO} + \underset{161.8}{2\,HBr} = \underset{223.4}{CuBr_2} + \underset{18.0}{H_2O}$$

The stoichiometric quantity of CuO [or $Cu(OH)_2$] is dissolved in aqueous hydrobromic acid and the solution is evaporated in vacuum over H_2SO_4.

II. $$\underset{199.6}{Cu(CH_3COO)_2 \cdot H_2O} + \underset{388.9}{3\,CH_3COBr} = \underset{223.4}{CuBr_2} + \underset{204.2}{2\,(CH_3CO)_2O} + \underset{60.1}{CH_3COOH} + \underset{80.9}{HBr}$$

Finely divided $Cu(CH_3COO)_2 \cdot H_2O$ (4.0 g.) is placed in a Pyrex tube (18 × 200 mm.) which is closed off with a rubber stopper

provided with a dropping funnel and a filtering tube. Agitation (magnetic stirrer) is started; 15 ml. of benzene is added, followed slowly by a 10% excess of CH_3COBr. The mixture is stirred for 30 minutes. The $CuBr_2$ precipitate is allowed to settle and the supernatant is siphoned off through the filtering tube. The reaction is brought to completion by treating the residue with additional benzene and CH_3COBr. The supernatant liquid is removed by filtration and the $CuBr_2$ is washed 3-4 times with anhydrous benzene. The product is dried at 150°C for two hours under nitrogen.

SYNONYM:

Cupric bromide.

PROPERTIES:

Black crystals, very deliquescent. M.p. 498°C, b.p. 900°C; d_4^{20} 4.710. Highly soluble in H_2O, yielding a green solution; solubility (15°C) 122 g./100 g. H_2O; soluble in acetone, alcohol and pyridine. Dry heating causes decomposition into CuBr and Br_2. Evaporation of an aqueous solution also causes decomposition (at the b.p.). Depending on the temperature, $CuBr_2$ crystallizes from aqueous solutions with two or four molecules of water of crystallization, yielding highly deliquescent, brownish-green crystals. Crystal structure: monoclinic. Heat of formation (25°C): −33.2 kcal./mole.

REFERENCES:

I. L. Vanino, Handbuch der präp. Chemie [Handbook of Preparative Chemistry], Part I, 2nd Ed., Stuttgart, 1921.
II. G. W. Watt, P. S. Gentile and E. P. Helvenston. J. Amer. Chem. Soc. 77, 2752 (1955).

Copper Oxychloride

$$CuCl_2 \cdot Cu(OH)_2$$

$$\underset{269.9}{2\,CuCl_2} + \underset{100.1}{CaCO_3} + \underset{18.0}{H_2O} = \underset{232.0}{CuCl_2 \cdot Cu(OH)_2} + \underset{111.0}{CaCl_2} + \underset{22.4\,l.}{CO_2}$$

Stoichiometric quantities of cupric chloride, calcium carbonate (marble) and water are allowed to react in a bomb tube for 48 hours at 200°C. The product is filtered, freed from unreacted $CuCl_2$ by washing with boiling alcohol, and dried in a desiccator.

Alternate method: A conc. solution of $CuCl_2$ is boiled for several hours with CuO. The liquid is decanted; the product is washed with acetone and dried [E. Hayek, Z. anorg. allg. Chem. 210, 241 (1933)].

PROPERTIES:

Dark yellowish-green powder, decomposed by boiling water. Crystal structure: monoclinic.

REFERENCE:

G. Rousseau. Compt. Rend. Hebd. Séances Acad. Sci. 110, 1262 (1890).

Copper (I) Oxide

Cu_2O

I.

$$\underset{(1\,H_2O)}{4\,Cu(CH_3COO)_2} + \underset{(1\,H_2O)}{N_2H_4} + 2\,H_2O$$

$$798.6 \qquad 50.1 \qquad 36.0$$

$$= 2\,Cu_2O + N_2 + 8\,CH_3COOH$$

$$286.2 \qquad 28.0 \qquad 480.4$$

A 20% hydrazine hydrate solution (3–5 ml.) is added to 50 ml. of concentrated copper acetate solution. The solution turns green, nitrogen evolves, and a yellow to orange precipitate of Cu_2O separates on standing. The product is washed with H_2O, followed by alcohol and ether. Care must be exercised to avoid an excess of hydrazine in the reduction, since such an excess causes reduction to metallic copper.

DropBooks

II.

$$4\,Cu + O_2 = 2\,Cu_2O$$

$$254.2 \qquad 22.4\,l. \qquad 286.2$$

Small copper plates (e.g., 5 mm. × 20 mm. × 10 μ) are hung from platinum wires placed in a vertical tubular furnace; the latter is then heated to 1000°C in an atmosphere of technical grade N_2 (1% O_2). While bringing to the desired temperature and cooling down, use only pure N_2. The reaction is completed after about 24 hours. The product composition corresponds approximately to Cu_2O [cf. C. Wagner and H. Hammen, Z. physik. Chem. B40, 197 (1938)].

Alternate methods: a) Equivalent amounts of CuO and Cu are heated in vacuum for five hours at 1000°C. The product is homogenized and reheated [F. W. Wrigge and K. Meisel, Z. anorg. allg. Chem. 203, 312 (1932)].

b) Reduction of Fehling's solution with hydrazine sulfate [M. C. Neuburger, Z. Physik 67, 846 (1931)].

c) Electrolysis of a weakly alkaline solution of NaCl at 80°C, using copper electrodes [B. B. Dey, A. Jorgarao, H. V. K. Udupa, S. Sampath and R. Viswanathan, J. Sci. Ind. Research (India) 13B, 219 (1954); Hira Lal, J. Sci. Ind. Research (India) 12B, 424 (1953)].

SYNONYM:

Cuprous oxide.

PROPERTIES:

Formula weight 143.08. Yellow powder. Red Cu_2O is identical with the yellow variety, the difference in color being caused by particle size. M.p. 1232°C; d_4^{25} 6.04. Insoluble in H_2O; soluble in aqueous ammonia, conc. aqueous hydrogen halide solutions, markedly soluble in alkali hydroxides. Soluble in dilute oxyacids, with formation of Cu and Cu^{++}. Crystal structure: type C3. Heat of formation (from $2\,Cu + \frac{1}{2}\,O_2$): −40.0 kcal./mole (25°C).

REFERENCES:

I. M. Straumanis and A. Cirulis, Z. anorg. allg. Chem. 224, 110 (1935).
II. H. Dünwald and C. Wagner, Z. phys. Chem. B22, 215 (1933); E. Engelhard, Ann. Phys. (V) 17, 501 (1933).

Copper (II) Oxide

CuO

The starting material, cupric nitrate, may be obtained by dissolving electrolytic copper in nitric acid and evaporating the solution to dryness on a steam bath:

$$\underset{(3\,H_2O)}{2\,Cu(NO_3)_2} = 2\,CuO + 4\,NO_2 + O_2$$

483.2 159.1 184.0 32.0

The cupric nitrate is dried in a drying oven, in which the temperature is raised very slowly from 90 to 120°C. After the material has been completely converted to the green, loose basic salt (24 hr.), it is boiled with water and filtered. The dried salt is first heated slowly to 400°C, resulting in removal of most of the nitric acid; it is then pulverized, slowly heated further to 850°C, and maintained at this temperature for one hour. It is again ground to a fine powder, reheated for several hours to about 700°C, and allowed to cool in a desiccator.

Alternate methods: a) Precipitation of $Cu(OH)_2$ from a $CuSO_4$ solution with ammonia, followed by calcination to CuO. The product is free of sulfate. Calcination temperature 600–700°C [A. A. Kazantsev, Khim. Zh., ser. B (Zh. Prikl. Khim.) 77, 1108 (1938)].

b) Oxidation of very pure thin copper foil at 1000°C in a stream of pure O_2 [H. H. von Baumbach, H. Dünwald and C. Wagner, Z. phys. Chem. B22, 226 (1933); K. Hauffe and P. Kofstand, Z. Elektrochem. 59, 399 (1955)].

c) Precipitation from $CuCl_2 \cdot 4\ H_2O$ with sodium hydroxide in the presence of CH_3OH [R. Fricke and J. Kubach, Z. Elektrochem. 53, 76 (1949)].

SYNONYM:

Cupric oxide.

PROPERTIES:

Formula weight 79.54. Black powder. M.p. 1336°C; d_4^{14} 6.315. Soluble in acids and ammonia. After calcination at high temperatures, soluble only in boiling conc. acids. Crystal structure: type B26. Heat of formation (25°C): −37.1 kcal./mole.

REFERENCE:

R. Ruer and J. Kuschmann, Z. anorg. allg. Chem. 154, 69 (1926).

Copper (II) Hydroxide

$Cu(OH)_2$

$$\underset{(5\ H_2O)}{CuSO_4} + 2\,NaOH = Cu(OH)_2 + Na_2SO_4$$

249.7	80.0	97.6	142.1

DropBooks

I. A solution of $CuSO_4 \cdot 5\ H_2O$ is treated at 70°C with 10% aqueous ammonia until a deep blue color appears. The solution is then allowed to react with the stoichiometric quantity of NaOH, yielding a precipitate which settles well. This is filtered, washed repeatedly with warm water, and dried in vacuum over conc. H_2SO_4.

II. Aqueous ammonia is added in drops to a boiling solution of $CuSO_4 \cdot 5\ H_2O$ until the initially green precipitate acquires a blue color. The crystalline basic sulfate thus obtained is filtered and carefully washed with water. It is then digested with a moderately concentrated NaOH solution, filtered, washed, and dried in vacuum over CaO or H_2SO_4.

SYNONYM:

Cupric hydroxide.

PROPERTIES:

Light blue, crystalline powder. Insoluble in H_2O; soluble in acids and aqueous ammonia; fairly soluble in concentrated NaOH. The crystalline form is stable at 100°C. Heating of the freshly

precipitated hydroxide results in conversion to black, water-containing cupric oxide. d_4^{20} 3.368. Heat of formation (18°C): −106.7 kcal./mole.

REFERENCES:

I. A. N. Agte and N. S. Golynko. Trudy Leningr. Khim.-Tekh. Inst. 8, 140 (1940).

II. L. Vanino and E. Engert. Chemiker-Ztg. 48, 144 (1927); B. Röttger. J. prakt. Chem. 73, 491 (1858); R. Fricke and J. Kubach. Z. Elektrochem. 53, 76 (1949).

Potassium Cuprate (III)

$KCuO_2$

A mixture of any available finely divided potassium oxide with CuO is heated to 400–500°C in carefully dried oxygen at 760 mm. Hg.

A) POTASSIUM OXIDE, KO_x

The sealed (20 cm. long) glass tube *d* containing distilled potassium is placed in the constricted side tube *b* of the apparatus depicted in Fig. 276; the system is evacuated and flame-dried, then filled with dry nitrogen; tube *a* is fixed so that it slopes somewhat toward *c*. Tube *d* is raised above *b* and its lower end broken in a stream of nitrogen; it is then replaced in *b* by means of a wire attached to hook *e*. The system is again evacuated; the potassium inside *b* is melted and allowed to flow into *a*, care being taken to avoid plugging of the gas inlet.

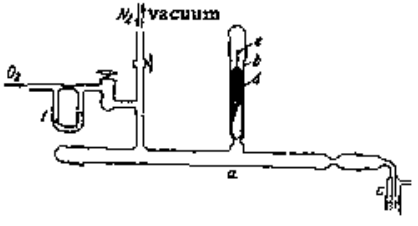

Fig. 276. Preparation of finely divided potassium oxide.

Oxidation of the potassium is achieved by admixing increasing amounts of oxygen to the nitrogen. The quantity of O_2 is adjusted by means of flowmeter *f*. When the reaction is complete, the resultant loose powder is homogenized in a vacuum ball mill (Fig. 55, p. 76) in a stream of dry N_2, and stored in sealed glass ampoules.

ANALYSIS:

Potassium is determined as $KClO_4$; the product may also be hydrolyzed and titrated as KOH.

B) REACTION OF KO_x WITH CuO

The potassium oxide prepared in (A) is ground with the stoichiometric amount of CuO (K:Cu = 1:1) in the vacuum ball mill mentioned above. The grinding is carried out with careful exclusion of moisture, and is continued until the powder clings to the walls. This usually takes 5–20 minutes. The inner ground joint s_2 of the ball mill is then connected to the outer joint s_2 of the transfer device shown in Fig. 277 in such a manner that the T-shaped transfer piece is horizontal. It contains a movable aluminum pin n which fits fairly loosely into opening s_3. To start with, s_3 is closed off with a ground cap. The mixture of oxides is transferred from the ball mill to the transfer device by shaking and knocking at the walls. The transfer device is disconnected from the mill in a stream of dry N_2 and joint s_2 is closed with a ground stopper; cap s_3 is then removed and s_3 is connected to joint s_3 on the side tube a of the main apparatus of Fig. 277. A silicon carbide boat k is located exactly below s_3. Stopper s_2 is removed, dry N_2 is introduced through s_4, and a small portion of the material is pushed into the boat by raising and lowering the aluminum pin n. Careful shifting of the boat followed by repeated movement of the pin allows the boat to be filled completely.

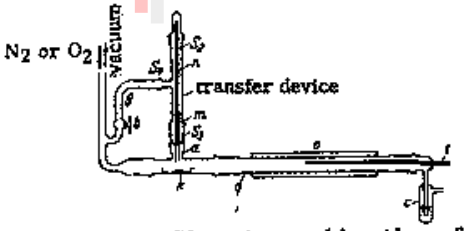

Fig. 277. Charging and heating of the KO_X–CuO mixture.

While the stream of dry N_2 continues to flow, the boat is shifted to reactor tube q, placed in furnace o (Fig. 277), which consists of an electrically heated quartz tube surrounded by a transparent protective tube. The mixture is heated to 450°C in very pure O_2; the formation of $KCuO_2$ is complete after 24 hours.

PROPERTIES:

Formula weight 134.64. Crystalline powder, steel blue to deep blue. Decomposes vigorously in water, yielding a brown-black

precipitate. Decomposes in dilute acids, evolving O_2 and forming cupric salts. Evolves chlorine and oxygen in conc. hydrochloric acid. Decomposes with loss of weight on heating above 500°C in a stream of oxygen. Nonmagnetic; shows a characteristic x-ray diffraction pattern.

REFERENCE:

K. Wahl and W. Klemm, Z. anorg. allg. Chem. 270, 69 (1952).

Schweizer's Reagent

I. Copper turnings are covered with 20% ammonia containing some NH_4Cl, and air is bubbled through the suspension. An azure-blue solution of $[Cu(NH_3)_4](OH)_2$ is formed. Evaporation of the solution in a stream of dry NH_3 yields long, azure-blue needles of $[Cu(NH_3)_4](OH)_2$.

II. Freshly precipitated $Cu(OH)_2$ is dissolved in 20% ammonia solution.

PROPERTIES:

Formula weight 165.68. Schweizer's reagent dissolves cellulose.

REFERENCE:

M. E. Schweizer, J. prakt. Chem. 72, 109, 344 (1857).

Copper (I) Sulfide

Cu_2S

$$\underset{127.1}{2\,Cu} + \underset{32.1}{S} = \underset{159.1}{Cu_2S}$$

I. A mixture of stoichiometric quantities of Cu and S is placed in a quartz tube, which is sealed in high vacuum. The tube is heated until the mixture melts.

II. An evacuated, sealed glass tube contains very pure Cu at one end, while the other is charged with the stoichiometric quantity of S purified by the method of von Wartenberg (p. 342). The reaction is complete after heating 1–2 days at 400°C.

Alternate methods: a) Cupric sulfide is heated in vacuum to the melting point of cuprous sulfide. The reaction is preferably

carried out in a graphite crucible inside an evacuated tube [E. Posnjak, E. T. Allen and H. E. Merwin, Z. anorg. allg. Chem. 94, 95 (1916)].

b) Cupric sulfide obtained by precipitation from a $CuSO_4$ solution with H_2S is reduced in a stream of H_2/H_2S. The optimum conditions are: a temperature of 700°C, a gas composition of 4.6% H_2 and 95.4% H_2S, and a reaction time of one hour. The product is crystalline and quite pure [N. P. Diyev and E. M. Yakimets, Izv. Ural. Fil. Akad. Nauk SSSR 1955, No. 3, 5; abstract in Chem. Abstr. 13,638a].

SYNONYM:

Cuprous sulfide.

PROPERTIES:

Blue to blue-black. M.p. 1127°C; d_4^{20} 5.6. Solubility (18°C): 4.95×10^{-5} g./100 g. H_2O. Very sparingly soluble in hydrochloric acid. Heat of formation (25°C): −19.6 kcal./mole.

Exists in two modification: β-Cu_2S (hexagonal) below 91°C, α-Cu_2S (type C 1) above 91°C. The latter exists only with a copper deficiency, the composition being approximately $Cu_{1.8}S$.

REFERENCES:

I. P. Rahlfs, Z. phys. Chem. (B) 31, 157 (1936); P. Ramdohr, Z. prakt. Geol. 51, 1 (1943).
II. C. Wagner, Private communication.

DropBooks

Copper (II) Sulfide

CuS

$$\underset{63.5}{Cu} + \underset{32.1}{S} = \underset{95.6}{CuS}$$

The sulfide precipitated when cupric salt solutions are treated with H_2S is not uniform. A better product is obtained from the reaction of a solution of sulfur in CS_2 with pure copper powder obtained from copper oxalate. Copper from CuO is unsuitable; it strongly absorbs H_2O vapor and thus still contains some oxygen.

A) COPPER OXALATE

A solution of $CuSO_4 \cdot 5\ H_2O$ in water is reacted with an equal volume of conc. H_2SO_4. The solution is brought to a boil, and a slight excess of boiling aqueous oxalic acid is introduced in a thin stream. The crystalline, easily filtered oxalate is repeatedly

washed with pure water, filtered through a filter crucible, and further washed until no acid can be detected.

B) COPPER POWDER

The copper oxalate is heated at 130°C to remove as much water of crystallization as possible. It is then placed in an electric furnace and heated to 320°C in a stream of purified H_2. The decomposition starts suddenly and is accompanied by a rise in temperature. Heating is continued at 220–260°C, and the product is then allowed to cool (both operations are conducted under a stream of H_2). The copper powder is stored under hydrogen.

C) COPPER SULFIDE

The copper powder obtained above is finely ground and covered with CS_2 in a beaker. Somewhat more than the theoretical amount of S is dissolved in a large volume of CS_2 and added to the contents of the beaker (the sulfur required may be obtained in sufficiently pure form by dissolving pure S in CS_2, filtering the solution through a glass filter crucible, and precipitating the filtrate with low-boiling petroleum ether). The resultant Cu_2S is transferred with the adhering CS_2 to a bomb and covered with twice the amount of S required for the formation of CuS. The bomb is filled as completely as possible with CS_2 and sealed. Then it is rotated along its long axis for four hours while surrounded with steam. The bomb is opened and contents filtered through a glass filter crucible and washed with CS_2; the residual, adhering CS_2 is removed in vacuum. The product is dried for 1–2 hours at 90–100°C in a vacuum of 0.1–1 mm. Hg.

SYNONYM:

Cupric sulfide.

PROPERTIES:

Black. M.p. (dec.) 200°C; d_4^{20} 4.6. Insoluble in H_2O, alcohol and dilute acids. Solubility (18°C): 33.6×10^{-6} g./100 g. H_2O. Somewhat soluble in solutions of $(NH_4)_2S$ and alkali polysulfides. Soluble without residue in KCN solution. Crystal structure: type B 18. Heat of formation (25°C): −12.1 kcal./mole.

REFERENCE:

K. Fischbeck and O. Dorner. Z. anorg. allg. Chem. 182, 228 (1928).

Copper (I) Selenide

Cu_2Se

$$\underset{127.1}{2\,Cu} + \underset{79.0}{Se} = \underset{206.0}{Cu_2Se}$$

Selenium vapor carried in a stream of nitrogen is passed over Cu placed in a porcelain boat. The Se is also in a porcelain boat located ahead of the Cu in the quartz reaction tube. A thermal gradient is obtained by means of two electric heaters which maintain the temperature of the Cu at about 400°C and that of the Se at about 300°C. A well-crystallized product is obtained.

Alternate methods: a) Heating a stoichiometric mixture of Cu and Se in an evacuated, sealed quartz tube [P. Rahlfs, Z. phys. Chem. (B) 31, 1957 (1936)].

b) Preparation of Cu_2Se and CuSe from Cu and Se in a Cu_2SO_4 solution [C. Goria, Gazz. Chim. Ital. 70, 461 (1940)].

c) Passage of H_2Se through solutions of Cu salts. Formation of CuSe and Cu_2Se [L. Moser and K. Atynski, Mh. Chemie 45, 235 (1925)].

d) Reduction of the basic selenite $CuO \cdot CuSeO_3$ [W. Geilmann and F. R. Wrigge, Z. anorg. allg. Chem. 210, 373 (1933)].

DropBooks

SYNONYM:

Cuprous selenide.

PROPERTIES:

Black. d_4^{21} 6.84. Exists in two modifications: tetragonal β-Cu_2Se (below 110°C), cubic α-Cu_2Se (above 110°C) (essentially a defect lattice deficient in copper). Heat of formation (25°C): −14.2 kcal./mole.

REFERENCES:

P. Rahlfs, Z. phys. Chem. (B) 31, 157 (1936); W. Borchert, Z. Kristallogr. 106, 5 (1945); G. Gattow and A. Schneider, Z. anorg. allg. Chem. 286, 296 (1956).

Copper (I) Telluride

Cu_2Te

$$\underset{127.1}{2\,Cu} + \underset{127.6}{Te} = \underset{254.7}{Cu_2Te}$$

Obtained by fusing electrolytic Cu with pure Te in a crucible under a protective layer of NaCl and KCl.

SYNONYM:

Cuprous telluride.

PROPERTIES:

Gray-blue, brittle; homogeneous; contains 33 and 35 atom % Te. M.p. about 900°C. d_4^{25} 7.338. Crystal structure: hexagonal (special type), defect lattice at $Cu_{<2}Te$.

REFERENCE:

H. Nowotny. Z. Metallforsch. (Metallkunde) 1, 40 (1946).

Copper (I) Sulfate

Cu_2SO_4

$$\underset{127.1}{2\,Cu} + \underset{196.2}{2\,H_2SO_4} = \underset{223.1}{Cu_2SO_4} + \underset{36.0}{2\,H_2O} + SO_2$$

Copper turnings are placed in conc. H_2SO_4 at a temperature of 200°C. The resultant green solution is added dropwise, through an asbestos filter, to an alcohol-ether mixture (1:1) or to methanol, causing Cu_2SO_4 to precipitate in the form of almost white crystals. The product is decanted, washed with alcohol, and dried in vacuum. It cannot be prepared by treating CuCl or CuI with H_2SO_4.

Alternate method: Double decomposition of Cu_2O with neutral dimethyl sulfate under anhydrous conditions [A. Recoura, Comptes Rendus Hebd. Séances Acad. Sci. 148, 1105 (1909)].

SYNONYM:

Cuprous sulfate.

PROPERTIES:

Nearly white crystals or grayish powder. Decomposes in water to $CuSO_4$ and Cu. Stable in dry air; decomposes slowly in moist air. Easily decomposed by heating; oxidizes at 200°C to CuO and $CuSO_4$. Heat of formation (25°C): −197.2 kcal./mole.

REFERENCE:

J. G. F. Druce and G. Fowles. Chem. News 137, 385 (1928).

Tetraamminecopper (II) Sulfate

$$[Cu(NH_3)_4]SO_4 \cdot H_2O$$

$$\underset{249.7}{CuSO_4 \cdot 5\,H_2O} + \underset{68.1}{4\,NH_3} = \underset{245.8}{[Cu(NH_3)_4]SO_4 \cdot H_2O} + \underset{72.1}{4\,H_2O}$$

A solution of 50 g. of finely divided $CuSO_4 \cdot 5\,H_2O$ in 75 ml. of conc. ammonia and 50 ml. of water is filtered and precipitated by slow addition of 75 ml. of alcohol. After standing for several hours in the cold, the crystals are filtered on a Büchner funnel, washed with a mixture of alcohol and conc. ammonia (1:1) and then with alcohol and ether, and dried by suction.

Large crystals may be obtained by covering a layer of alcohol with a layer of an ammonia solution of $CuSO_4$ (G. Bornemann, Anorgan. Präparate [Inorganic Preparations], Leipzig, 1926, p. 156).

SYNONYM:

Cuprammonium sulfate.

PROPERTIES:

Deep blue crystals. d_4^{20} 1.81. Solubility (21.5°C): 18.5 g./100 g. H_2O. Decomposes in air. Loses H_2O and 2 NH_3 on heating to 120°C; the remaining ammonia is evolved at 160°C.

DropBooks

REFERENCES:

H. and W. Biltz. Übungsbeispiele aus der anorg. Chemie [Exercises in Inorg. Chem.], Leipzig, 1920; F. Mazzi. Acta Cryst. 8, 137 (1955); M. Simerská. Czechosl. J. Phys. 4, 3 (1954).

Copper (I) Nitride

$$Cu_3N$$

This compound is prepared by treating CuF_2 with NH_3.

A) STARTING MATERIALS

1. According to L. Balbiano [Gazz. Chim. Ital. 14, 78 (1884)] $CuF_2 \cdot 2\,H_2O$ is prepared by dissolving CuO in 40% hydrofluoric acid, precipitating the fluoride with alcohol, and drying in a vacuum.
2. NH_4F is dried in vacuum over NaOH.
3. NH_3 and N_2 are carefully dried.

B) DEHYDRATION OF $CuF_2 \cdot 2H_2O$

About 1.5 g. of a mixture of 5 parts of $CuF_2 \cdot 2\,H_2O$ and 1 part of NH_4F, in a corundum boat placed in a quartz tube set in an electric resistance furnace, is slowly heated for two hours to 280°C in a stream of N_2. (The NH_4F serves to depress hydrolysis during the dehydration.)

C) PREPARATION OF Cu_3N

The anhydrous CuF_2, at 280°C (see above), is immediately reacted for three hours at the same temperature with a fast stream of NH_3. Heating above 300°C gives products deficient in nitrogen.

SYNONYM:

Cuprous nitride.

PROPERTIES:

Formula weight 204.63. Dark green powder, stable in air at room temperature; oxidizes at 400°C in a stream of O_2 with pronounced incandescence. Decomposes spontaneously in vacuum at about 450°C. Soluble in dilute mineral acids and conc. hydrochloric acid with formation of the corresponding ammonium salt and partial formation of Cu metal. Decomposes violently with conc. H_2SO_4 and HNO_3. d_4^{25} 5.84. Crystal structure: type $D0_3$. Heat of formation (25°C): +17.8 kcal./mole.

REFERENCES:

R. Juza and H. Hahn, Z. anorg. allg. Chem. 239, 282 (1938); 241, 172 (1939); R. Juza, Ibid. 248, 118 (1941).

Copper (II) Azide

$$Cu(N_3)_2$$

$$\underset{(3\,H_2O)}{Cu(NO_3)_2} + 2\,NaN_3 = Cu(N_3)_2 + 2\,NaNO_3$$

241.6 130.0 147.6 170.0

A solution of 5 g. of $Cu(NO_3)_2 \cdot 3\,H_2O$ in 200 ml. of H_2O is treated in the cold with 50 ml. of a solution containing 2.5 g. of NaN_3. The resultant precipitate is suction-filtered and washed several times with cold water. The wet product is left to stand 24 hours in 50 ml. of a 2% solution of hydrazoic acid, suction-filtered, washed with alcohol and ether, and dried at room temperature. The yield is 2.5 g. of azide in the form of a brown-black mass with a reddish shine.

Alternatively, finely powdered basic $CuCO_3$ may be treated with an excess of 2% HN_3, after which the workup is the same as above.

Alternate methods: a) Reaction between $Cu(NO_3)_2 \cdot 3\,H_2O$ and $LiN_3 \cdot H_2O$ in alcoholic solution and decomposition of the $Cu(N_3)_2 \cdot 2\,NH_3$ [M. Straumanis and A. Cirulis, Z. anorg. allg. Chem. 251, 315 (1943)].

b) Determination of azide nitrogen according to F. Feigl and E. Chargaff, Z. anal. Chem. 74, 376 (1928).

SYNONYM:

Cuprous azide.

PROPERTIES:

Black-brown powder or black-brown, opaque crystal needles, depending on the method of preparation. Very sparingly soluble in H_2O and organic solvents. Readily soluble in acids, including CH_3COOH, and in ammonia. Decomposes on heating in air into Cu and N_2. Can be easily reduced to white CuN_3 in an aqueous solution of hydrazine. Crystal structure: orthorhombic.

Explosive properties: Harmless when moist, quite sensitive to rubbing when dry or moistened with ether. Explodes when placed in a flame. Six times stronger than $Pb(N_3)_2$ and 450 times stronger than mercury fulminate when used as a detonator.

DropBooks

REFERENCE:

M. Straumanis and A. Cirulis. Z. anorg. allg. Chem. 251, 315 (1943).

Copper Phosphide

Cu_3P

$$3\,Cu + P = Cu_3P$$
$$190.6 \quad 31.0 \quad 221.6$$

Stoichiometric amounts of Cu and red P are heated for 20 hours at 640°C in an evacuated, sealed Vycor glass tube. The reaction product is homogenized, melted in a sealed quartz tube and heated for five hours at 1000°C.

PROPERTIES:

Silvery, shiny material with metallic appearance. Insoluble in nitric acid. d_4^{25} 7.147. Crystal structure: hexagonal. Heat of formation (25°C): — 36.0 kcal./mole.

REFERENCE:

H. Haraldsen, Z. anorg. allg. Chem. 240, 337 (1939).

Copper Diphosphide

CuP_2

$$\underset{221.6}{Cu_3P} + \underset{154.9}{5\,P} = \underset{376.5}{3\,CuP_2}$$

A mixture of Cu_3P with the calculated amount of red phosphorus is heated in a quartz tube for 24 hours at 600°C.

PROPERTIES:

Formula weight 125.49. Gray-black, grainy powder. Slowly dissolves in boiling nitric acid (1.2). d_4^{25} 4.201. Heat of formation (25°C): −23.5 kcal./mole.

REFERENCE:

H. Haraldsen, Z. anorg. allg. Chem. 240, 337 (1939).

Basic Copper Carbonates

$CuCO_3 \cdot Cu(OH)_2$ (Green Cupric Carbonate)

$$\underset{(3\,H_2O)\ 483.2}{2\,Cu(NO_3)_2} + \underset{212.0}{2\,Na_2CO_3} + \underset{18.0}{H_2O} = \underset{221.2}{CuCO_3 \cdot Cu(OH)_2} + \underset{44.0}{CO_2} + \underset{340.0}{4\,NaNO_3}$$

An aqueous solution of $Cu(NO_3)_2 \cdot 3\,H_2O$ is allowed to react at room temperature with a solution containing the equivalent amount of sodium or potassium carbonate. The greenish blue, partially colloidal precipitate of varying composition that forms is gradually transformed under the mother liquor into crystalline $CuCO_3 \cdot Cu(OH)_2$. Instead of $Cu(NO_3)_2 \cdot 3\,H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$ or $CuSO_4 \cdot 5\,H_2O$ may be used.

Alternate methods: a) Precipitation of 100 ml. of 1N $CuSO_4$ with 110 ml. of 1N Na_2CO_3, followed immediately by filtering, washing with warm water, and drying after standing for 24 hours [M. Grüger, Z. anorg. allg. Chem. 24, 127 (1900)].

b) Hot $CuSO_4$ solution is precipitated with sodium hydroxide. The precipitate is decanted and washed until the solid is free of alkali. It is then dissolved in acetic acid, the solution is evaporated to dryness, and the residue is taken up in water and added to a 100°C solution containing 4/5 of the equivalent quantity of K_2CO_3. The supernatant is decanted and the precipitate is washed with hot water and dried [W. C. Reynolds, Proc. Chem. Soc. (London) 190, 53 (1897/98)].

PROPERTIES:

Malachite-green powder, insoluble in H_2O, soluble in aqueous ammonia. On boiling in water, particularly when the latter contains alkali carbonate, deposits brown oxide. Stable to 150°C in the absence of alkali, decomposes at 220°C. Unstable toward H_2S. d_4^{25} 3.85.

REFERENCE:

G. Bornemann. Anorg. Präparate [Inorganic Preparations], Leipzig, 1926, p. 156.

DropBooks

$2\,CuCO_3 \cdot Cu(OH)_2$ (Blue Cupric Carbonate)

$$\underset{(3\,H_2O)}{3\,Cu(NO_3)_2} + \underset{300.3}{3\,CaCO_3} + \underset{18.0}{H_2O} = \underset{344.7}{2\,CuCO_3 \cdot Cu(OH)_2} + \underset{492.3}{3\,Ca(NO_3)_2} + \underset{22.4\,l.}{CO_2}$$

A solution of copper nitrate is mixed with an excess of pieces of chalk, and the mixture is placed in a large-diameter tube of strong glass connected to a mercury manometer. The tube is then sealed. The azurite forms at room temperature when the liberated CO_2 creates a pressure of 5–8 atm.

Alternate methods: a) From precipitated green basic copper carbonate under a CO_2 pressure of 4 atm. The reaction is markedly accelerated by the addition of azurite [V. Auger, Comptes Rendus Hebd. Séances Acad. Sci. 158, 944 (1914)].

b) A soluble copper salt is added in portions to a solution containing Na_2CO_3, $NaHCO_3$ and suspended blue copper carbonate. A new portion is added only after the previous one has been converted from the green basic carbonate to the blue [V. Auger, loc. cit.].

c) Formation from $CuCO_3 \cdot Na_2CO_3 \cdot 3\,H_2O$ (from saturated $NaHCO_3$ solution and precipitated basic $CuCO_3$) and moist CO_2 at 40 atm. [V. Auger, loc. cit.].

PROPERTIES:

Azure-blue crystalline powder. M.p. (dec.) 220°C; d_4^{20} 3.88. Insoluble in water. Converts to the green compound in humid air. Soluble in ammonium salt solutions. Crystal structure: orthorhombic.

REFERENCE:

H. J. Debray. Comptes Rendus Hebd. Séances Acad. Sci. 49, 218 (1859).

Copper (I) Acetylide

$$Cu_2C_2 \cdot H_2O$$

$$\underset{198.0}{2\,CuCl} + \underset{22.4\,l.}{H_2C_2} = \underset{169.1}{Cu_2C_2\,(H_2O)} + \underset{72.9}{2\,HCl}$$

Pure CuCl (10 g.) is added in vacuum to a solution of 30 g. of NH_4Cl in 100 ml. of H_2O; it dissolves after addition of 50 ml. of conc. ammonia. A solution of 20 g. of hydroxylammonium chloride in 100 ml. of H_2O is then added, and the entire mixture is diluted with 150 ml. of H_2O. The solution becomes completely colorless after a few minutes. It is then siphoned into an evacuated vessel, and acetylene is introduced. The acetylene (from a steel cylinder) passes through a purification train consisting of sealed wash bottles equipped with fritted glass plates and filled (in succession) with $HgCl_2$ solution, 2N NaOH, $Cu(NO_3)_2$ in nitric acid and 2N H_2SO_4, followed by two wash bottles filled with 2% leuco-indigo carmine solution (made from indigo carmine and zinc dust), for the detection and absorption of O_2, and a glass-bead trap for catching any entrained liquid droplets. Upon contact with the cuprous salt solution, acetylene produces a bright red, flocculent and very voluminous precipitate. The product is suction-filtered on a fritted-glass funnel and washed with boiled water and acetone, all operations being carried out in vacuum. After thorough suction-drying, it is dried at 100°C (in high vacuum) in a drying pistol. The product contains about 95% $Cu_2C_2 \cdot H_2O$ and is stored in sealed ampoules filled in high vacuum.

PROPERTIES:

Brownish-red powder. Insoluble in H_2O, soluble in HCl and KCN solutions. On heating with HCl, moist, freshly prepared $Cu_2C_2 \cdot H_2O$ decomposes into C_2H_2 and CuCl (and a small amount of vinyl chloride). Oxidizes in air to Cu_2O, C and H_2O, the color changing to dark brown.

REFERENCES:

R. Klement and E. Köddermann-Gros. Z. anorg. Chem. 254, 201 (1947); L. Ilosvay. Ber. dtsch. chem. Ges. 32, 2697 (1899).

Paris Green (Copper Acetoarsenite)

$$4\,CuO + 3\,As_2O_3 + 2\,CH_3COOH = 3\,Cu(AsO_2)_2 \cdot Cu(CH_3COO)_2 + H_2O$$
$$315.2 \qquad 593.5 \qquad 120.1 \qquad 1013.7 \qquad 18.0$$

Cupric oxide is heated with 8% acetic acid, As_2O_3 is added, and the mixture is refluxed for two hours. The product is allowed to cool for half an hour, filtered, washed and dried.

Alternate method: Dilute acetic acid is allowed to react with an excess of freshly precipitated $Cu(OH)_2$ and the product is separated by filtration. Dilute acetic acid is added to a solution of As_2O_3 in boiling NaOH until the color of phenolphthalein disappears. The hot solutions are mixed (mole ratio of $CuO:As_2O_3 = 4:3$) and allowed to stand for several days [S. Avery, J. Amer. Chem. Soc. 28, 1159 (1906)].

PROPERTIES:

Emerald green, crystalline powder, stable to air and light. Insoluble in H_2O. Decomposes on prolonged heating in H_2O. Unstable in acids, bases and toward H_2S. Toxic.

REFERENCE:

G. D. Luchinskiy and U. F. Churilkina. Zh. Prikladnoy Khim. 13, 558 (1940).

Fehling's Solution

SOLUTION 1

34.6 g. of $CuSO_4 \cdot 5\,H_2O$ dissolved in 500 ml. of H_2O.

SOLUTION 2

173 g. of crystalline potassium sodium tartrate (Rochelle salt) and 53 g. of NaOH are dissolved in H_2O and diluted to 500 ml.

Equal volumes of the two solutions are mixed before use.

DropBooks

PROPERTIES:

Deep blue solution, reduced to Cu_2O on heating with reducing agents (sugar test in urine).

REFERENCE:

J. D'Ans and E. Lax, Taschenbuch für Chemiker und Physiker [Pocket Book for Chemists and Physicists], Berlin, 1943, p. 1779.

Very Pure Silver

Crude silver (e.g., from silver residues, see p. 1029) is dissolved in conc. nitric acid, and the diluted solution is precipitated in the cold with a solution of very pure NaCl. The precipitate is washed several times with cold water and dissolved in freshly prepared ammonia solution. After several hours of standing, the solution is filtered. Silver chloride is precipitated from the filtrate with very pure nitric acid, washed with H_2O until no further nitrate can be detected, and reduced in a silver dish with invert sugar* and NaOH (from Na metal) at 60°C, with sucrose and NaOH, or with a boiling alkaline solution of formaldehyde (the formaldehyde should be distilled prior to the preparation; sugar solutions should be filtered through bone charcoal and recrystallized). The resultant silver slurry is filtered, carefully washed free of chloride ion with water, dried and melted down to small ingots over pure CaO. If the metal is heated no longer than absolutely necessary for melting, and if the resultant metal grains are cooled in a reducing flame, the silver obtained is quite pure; it contains about 0.001% S and traces of C, AgCl and O.

The silver obtained in this manner is further purified by electrolysis. The greater part of the grains is used as the anode (fritted glass finger filled with the Ag) against a cathode of pure silver (wire or sheet). The electrolyte is a 10% $AgNO_3$ solution prepared from the remaining melted silver and very pure nitric acid. The power supply lead is a strip of fine sheet silver whose upper surface is protected by a layer of asphalt or Bakelite lacquer. The electrolysis is carried out at a constant voltage of 1.39 v. across the terminals. The silver flakes depositing on the cathode are removed from time to time, carefully washed, dried and fused to ingots in a stream of pure hydrogen in a boat made of very pure CaO.

*A 1:1 mixture of dextrose and levulose.

PROPERTIES:

Atomic weight 107.88. M.p. 960.5°C, b.p. 2170°C; d_4^{20} 10.497. Crystal structure: type A 1.

REFERENCES:

O. Hönigschmid and R. Sachtleben. Z. anorg. allg. Chem. 195, 207 (1931); Th. W. Richards and R. C. Wells. Z. anorg. allg. Chem. 47, 56 (1905); O. Hönigschmid, E. Zintl and M. Linhard. Z. anorg. allg. Chem. 136, 263 (1924).

Silver Powder

Pure AgCl is stirred with water, allowed to react with sodium hydroxide, and reduced with glucose, which is added to the boiling suspension in small portions. Samples are removed from time to time, filtered and carefully washed. If the Ag yields a completely clear solution on heating in chloride-free HNO_3, the reduction is complete. The medium must be kept alkaline throughout the reaction; an excess of glucose should be avoided. The product is filtered, washed free of base, and dried at 100°C.

Alternate methods: a) Reduction of AgCl with aqueous formaldehyde [L. Vanino, Ber. dtsch. chem. Ges. 31, 1764 (1898)].

b) Heating finely powdered Ag_2O to 500°C [F. Jirsa and J. Jelinek, Z. anorg. allg. Chem. 158, 63 (1926)].

c) Reduction of Ag_2O with H_2O_2 and drying at 250°C [F. Jirsa and J. Jelinek, loc. cit.].

PROPERTIES:

Gray, crumbling powder. According to Vanino, the product of the reduction is a loose, black powder.

REFERENCE:

G. Bornemann. Anorg. Präparate [Inorganic Preparations], Leipzig, 1926, p. 161.

Silver from Residues

I. The collected residues are allowed to react with hydrochloric acid (1:1). The precipitate is allowed to settle and the supernatant is siphoned off. The precipitate is washed free of iron by repeated decantation with hydrochloric acid and water, filtered with suction,

placed in a large porcelain dish, mixed with HCl (1:1), and reduced with Zn rods with stirring. After disappearance of the white particles of AgCl, the Ag slurry is washed free of acid and Zn with hot water and filtered. The washings should be tested for the presence of Zn. The resultant silver slurry can be processed further either to Ag or $AgNO_3$ (when only pure AgCl is required, an ammonia solution of the salt may be reduced with 20% hydrazine hydrate).

a) The silver slurry is dried and fused with a small quantity of borax in a Hessian crucible. The fused Ag is made into granules by careful pouring into water.

b) The silver slurry is dissolved in nitric acid (1:1); the solution is filtered and evaporated in a porcelain dish on a steam bath until crystallization. The last traces of nitric acid are removed by drying in a vacuum or by fusion.

Alternate methods: The silver obtained from the reduction with Zn is dissolved in dilute nitric acid. The solution is filtered and AgCl is precipitated by addition of dilute hydrochloric acid to the hot solution. The precipitate is filtered, carefully washed with warm water, and dried. Then 20 parts of AgCl are mixed in a mortar with 10 parts of Na_2CO_3 and 3 parts of KNO_3. The mixture is placed in a red-hot Hessian crucible. The reduction proceeds according to $2\ AgCl + Na_2CO_3 = 2\ Ag + 2\ NaCl + CO_2 + \frac{1}{2}\ O_2$. The AgCl may also be added in portions to the mixture heated slightly above 960°C. A melt of Ag is formed immediately. The Ag ingot is cleaned by boiling in water containing sulfuric acid (G. Bornemann, Anorg. Präparate [Inorganic Preparations], Leipzig, 1926, p. 160).

REFERENCES:

Handbuch für das Eisenhüttenlaboratorium [Handbook for the Iron Works Laboratory], Vol. I, p. 317 (1939). F. Specht. Quantitative anorganische Analyse in der Technik [Quantitative Inorganic Analysis in Engineering], 1953.

II. SILVER FROM PHOTOGRAPHIC SOLUTIONS

The photographic solution is made alkaline with ammonia and allowed to react with a slight excess of ammonium sulfide. The mixture is allowed to stand overnight and the supernatant liquid is siphoned off. The residue is suction-filtered and washed with water. The precipitate, after addition of a small amount of anhydrous borax, is placed in a Hessian crucible, dried and calcined at 960°C. The borax is leached out of the product with hot water.

Alternate methods: a) Zinc rods are placed in exhausted fixing solutions and allowed to stand for about one week with frequent

agitation. The precipitated Ag slurry is filtered off and cupellated with lead (H. Grubitsch, Anorg. präparative Chemie [Inorganic Preparative Chemistry], Vienna, 1950, p. 454; for description of cupellation, see also Hackh's Chemical Dictionary, 3rd ed., The Blakiston Co., Philadelphia-Toronto, 1944).

b) The pH of the solution is adjusted to 6.9-7.2 with soda, and $CuSO_4$ or $Al_2(SO_4)_3$ is added. Silver precipitates with the corresponding hydroxide (when the Ag is not present as AgCl, $FeCl_3$ is added). The voluminous precipitate is treated after 3-4 days with sulfuric acid of increasing concentration (up to 96%), which removes hydroxides, gelatin and other impurities and concentrates the Ag to 20-50% of the total. The Ag is fused in a crucible after adding some borax (U.S. Pat. 2,131,045).

REFERENCE:

Handbuch für das Eisenhüttenlaboratorium [Handbook for the Iron Works Laboratory], Vol I, p. 318 (1939).

Silver Mirrors

DropBooks

Of the two methods given below, the first is best for flat surfaces, while the second is used for concave surfaces, such as vacuum jackets. With variations, however, they may also be used in other applications. Careful and thorough cleaning of the mirror surface (glass, quartz, porcelain, mica, plastic, etc.) is a necessary condition for any successful silvering effort.

1. A) PREPARATION OF THE MIRROR SURFACE

The silver coating on old mirrors is dissolved with nitric acid and the surface is rinsed with water. The hands are scrubbed with soap, and the soap foam is transferred to the surface, which is then scrubbed for some time with the foam. Scrubbing is continued while the surface is rinsed, first with tap water, then with distilled water. In the end, the units surface must be perfectly wetted by the water. If any greasy, water-repellent area remains, the entire operation must be repeated. After rinsing, the piece to be mirrored is placed in a dish of distilled water.

If it is desired to polish the silver mirror after deposition, the surface is first covered with a thin paste prepared from equal parts of alcohol, ammonia and precipitated calcium carbonate, and the paste is rubbed in vigorously with cellulose pulp. This cleaning mixture may then be removed with some fresh cellulose.

B) PREPARATION OF THE SOLUTION

The following are weighed into three clean test tubes: 1) 5 ± 0.1 g. of $AgNO_3$, 2) 1.1 ± 0.05 g. of $AgNO_3$, 3) 0.9 ± 0.05 g. of Rochelle salt. The second and third of these compounds are dissolved in a few milliliters of distilled water.

The following are held in readiness: two dark brown bottles (500 ml.) with ground stoppers; three beakers or Erlenmeyer flasks with capacities of a) 800, b) 300, c) 100 ml.; a 20-ml. burette; a glass funnel.

C) SILVER SOLUTION

The 5 g. of $AgNO_3$ (test tube 1) is dissolved in 50–100 ml. of distilled water in vessel *b*; one third of the solution is held in reserve in *c*. Ammonia is added (with vigorous swirling) from the burette to the larger portion in *b* until the resultant deep brown precipitate just dissolves. Some $AgNO_3$ solution is then added from the reserve, ammonia is again added in drops, and the procedure is repeated until the reserve has been exhausted. The last solution added should be $AgNO_3$, and the mixture should be somewhat turbid. If the solution is clear at the end of the operation, a few crystals of $AgNO_3$ are dissolved in distilled water and added to the mixture until turbidity sets in. The Ag solution is diluted to 500 ml. with distilled water and transferred without filtering to one of the brown bottles. Thus protected against light, it may be stored almost indefinitely.

D) REDUCING SOLUTION

The solution of Rochelle salt (test tube 3) is added to 500 ml. of distilled water in vessel *a*; the mixture is brought to a boil, and the $AgNO_3$ solution from test tube 2 is added, first in drops (the addition causes a boiling point elevation and thus a delay in boiling—do not add the $AgNO_3$ too fast!), then more rapidly. The resultant brown-colored turbidity gradually transforms into a greenish-gray precipitate. The solution is boiled over a small flame for six additional minutes, filtered and stored in the second brown bottle. In this bottle the solution is stable for several months.

E) SILVERING

Small mirrors are best made in a thoroughly cleaned crystallizing dish or a photographic developing tray. Larger mirrors are best prepared by creating a 5-cm.-high leakproof rim of paraffined paper at the edge of the surface, so that the surface itself serves as the bottom of the dish.

Equal volumes of the silver-containing and reducing solutions are measured out in a graduated cylinder in amounts sufficient to cover the mirror surface with a layer of liquid 1 cm. deep. The mixture is then immediately poured on to the surface and the dish is vigorously rocked. A bluish, rapidly thickening deposit is formed after a few minutes on the mirror and the glass walls. The solution becomes turbid and small silver particles appear on the surface of the liquid. The solution is poured off, the mirror rinsed with distilled water, and the silvering process repeated with fresh solution. Finally, the silvered piece is rinsed with distilled water followed by alcohol, and the mirror is allowed to dry while standing on end. It is advisable to grip the mirror with lab. tongs or forceps and not to touch it with the fingers.

In the case of mirrors silvered on the back, the silver layer is protected with a lacquer coating (shellac, varnish). The Ag precipitated on the glass side is removed with a cotton pad moistened with highly diluted nitric acid.

F) POLISHING

The operation is carried out on the day following the silvering. A piece of dust-free chamois leather is tightened around a ball of wool ("polishing ball"). The surface is then carefully gone over with the ball and is then rubbed with increasing pressure. If this does not produce the desired result, some jeweler's rouge is spread on the ball, the excess is brushed off, and polishing is continued.

The mirror prepared as above has a golden sheen (on the back side).

II. A) PRETREATMENT

The glass surface to be treated, such as the inner space of a jacket, is cleaned for 30 minutes at 60°C with freshly prepared cleaning solution and is then thoroughly rinsed with water. This is followed by a 10-minute treatment with 1.4% hydrofluoric acid and another rinse with water. Then the surface is treated for 10 minutes with technical grade conc. nitric acid (d 1.52) and rinsed with water; the final rinse is distilled water.

B) SILVERING

The following three solutions are prepared separately:

1) 50 g. of $AgNO_3$ in two liters of water; stored in the dark in a ground-joint bottle;

2) 90 g. of very pure, chlorine-free KOH in two liters of water; rubber-stoppered bottle;

3) 80 g. of sugar in 800 ml. of water; a mixture of 100 ml. of 96% alcohol and 3.5 ml. of very pure, chlorine-free nitric acid (d 1.42) is added to this solution, which is then stored for at least one week before use in a ground-joint bottle.

The three solutions (16:8:1) are mixed as follows: conc. ammonia is added in drops with stirring to solution (1) until the initially formed precipitate just dissolves. Solution (2) is then added, yielding a dark brown to black precipitate (a green precipitate indicates a deficiency of ammonia and the material must be rejected). If the precipitate is of the right color, ammonia is again added slowly with stirring until the precipitate just disappears. A slight excess of ammonia delays the deposition of silver in the next stage, but does not prevent it. The resultant mixture of (1) and (2) may be stored, at most, for one hour. Solution (3) is added immediately before use. The deposition of silver lasts 10 to 30 minutes, depending on the excess of ammonia. Its completion is recognizable by the appearance of a flocculent precipitate. The solution must be removed at this point to avoid harm to the mirror. The surface is thoroughly rinsed with distilled water to remove all residues (including silver slurry) and dried, preferably in vacuum. The silver layer and the glass do not separate on heating to 450°C in a high vacuum of 10^{-5} mm., which is particularly important in silvering of vacuum jackets for distillation columns.

REFERENCES:

I. W. Bothe. J. prakt. Chem. 42, 191 (1863); R. Böttger. Polytechn. Notizbl. 38, 217 (1883); 39, 324 (1884); H. Kreusler, Die Sterne 9, 42 (1929); E. von Angerer. Techn. Kunstgriffe [Industrial Techniques], 5th ed., Braunschweig, p. 61.
II. P. W. Schenk. Private communication.

Colloidal Silver

A mixture of 200 ml. of 30% $FeSO_4$ solution, 280 ml. of 40% sodium citrate, and about 50 ml. of 10% NaOH is added to 200 ml. of 10% $AgNO_3$ solution. The resultant colloidal silver precipitate is allowed to settle and washed 4–5 times with 10% ammonium nitrate solution and finally twice with 96% alcohol. The mixture is centrifuged and the product carefully dried on a water bath or in a desiccator.

Alternate methods: a) A 0.001N $AgNO_3$ solution (100 ml.) is treated with a few drops of freshly prepared tannin solution and one drop of 1% sodium carbonate solution. Heating the mixture results in formation of a sol (W. Ostwald, Kleines Praktikum der Kolloidchemie [Lab. Manual for Colloid Chem.], 7th ed., 1930, p. 4).

b) A warm 0.001N solution of $AgNO_3$ is reduced by dropwise addition of 0.005% hydrazine hydrate solution (Ag sol according to Gutbier, cited in W. Ostwald, loc. cit.).

c) Silver sol by electrical atomization: Two silver rods, 2-3 mm. in diameter, are bent at right angles 2 cm. from their ends and the bent sections immersed in a beaker with distilled water so that they form a U figure. A current of 4-6 amp. should flow at 110 volts through the short-circuited electrodes (rheostat control). Clouds of colloidal Ag are formed when an electric arc is passed through the gap between the two ends. Addition of a few drops of 2% sodium carbonate solution is recommended [G. Bredig, Angew. Chem. 951 (1898)].

PROPERTIES:

Black, grainy powder containing about 97% Ag. Soluble in water, yielding a red-brown to black, extremely finely divided Ag sol.

REFERENCE:

M. Carey Lea. Amer. J. Sci. 37, 476 (1889).

DropBooks

Silver Iodide

AgI

$$\underset{169.9}{AgNO_3} + \underset{166.0}{KI} = \underset{234.8}{AgI} + \underset{101.1}{KNO_3}$$

At atmospheric pressure silver iodide exists in three modifications: α-form (cubic, type B3), β-form (hexagonal, type B4) and γ-form (cubic, type B3). At room temperature, the rate of interconversion between the α- and β-forms is so low that the two forms are stable when stored alone or as a mixture. The silver iodide precipitated from solutions usually consists of a mixture of these two modifications. When physical uniformity of the product is not a factor, chemically pure AgI may be prepared in large quantities by the following method.

Very pure KI (83 g.) is dissolved in 8.3 liters of distilled water, and 85 g. of very pure $AgNO_3$ in 8.5 liters of water. The KI solution is added, with constant stirring, to the $AgNO_3$ solution. A milky liquid is initally formed; flocculation occurs only later. The supernatant is siphoned off after standing 2-3 hours, the precipitate is transferred to a three-liter bottle, two liters of distilled water is added, and the mixture is shaken vigorously to

disperse the small clumps of iodide. The flocculent precipitate settles rapidly, and the clear supernatant may be siphoned off after about five minutes. The product is cleaned by decantation until all the KNO_3 has been removed. The wash water is allowed to remain in contact with the precipitate overnight to remove all of the possibly adsorbed electrolyte (which is hard to dislodge). (Test for KNO_3: evaporation to dryness of 200 ml. of the wash water in a platinum dish. Blank test with the distilled water used for washing.) The precipitate is placed on a piece of hard filter paper and dried at 110–120°C. The dry AgI is easily ground to a fine powder.

The mixing of the solutions and the washing operations must be carried out in the absence of daylight. The product may be exposed to daylight only when it is completely free of impurities.

PROPERTIES:

Yellow, crystalline. M.p. 556.8°C, b.p. 1506°C. Insoluble in H_2O; solubility (25°C): $0.25 \cdot 10^{-6}$ g./100 g. H_2O; almost insoluble in ammonia; appreciably soluble in conc. hydriodic acid and conc. solutions of alkali iodides, particularly when hot; soluble in $Na_2S_2O_3$ solution. Heat of formation −14.95 kcal. per mole.

HEXAGONAL β-AgI

Silver iodide as precipitated above is dissolved in a conc. solution of potassium iodide. The solution is filtered and poured into water. The AgI precipitates as a thick flocculate. It is washed with water (by decantation) until the iodide ion is no longer detectable by the $AgNO_3$ test. The AgI is filtered and dried at room temperature.

$d_4^{20°}$ 5.696; crystal structure: type B4.

CUBIC α-AgI

a) Cubic AgI is always formed when hexagonal or mixed AgI is pulverized.

b) Silver iodide is dissolved in a conc. solution of $AgNO_3$. The solution is filtered and poured into water. Fine-grained, slowly coagulating AgI is formed. It is washed by decantation until the silver ion cannot be detected in the wash water. The mixture is filtered and the product dried at room temperature.

$d_4^{20°}$ 5.680; crystal structure: type B3.

REFERENCE:

H. H. Kolkmeijer and J. W. A. van Hengel. Z. Kristallogr. A 88, 317 (1934).

Silver Chlorate

$AgClO_3$

$$\underset{169.9}{AgNO_3} + \underset{106.4}{NaClO_3} = \underset{191.3}{AgClO_3} + \underset{85.0}{NaNO_3}$$

Solutions of 170 g. of $AgNO_3$ and 106 g. of $NaClO_3$, each dissolved in 100 ml. of 85°C water, are combined and cooled to 0°C. The supernatant is carefully decanted and 50 ml. of H_2O (0°C) is added to the residue. The resultant crystals are suction-filtered; they are 95% pure.

A purer product may be obtained by dissolving the residue remaining after the above decantation in 125 ml. of H_2O at 90°C, cooling to 0°C, and suction-filtering. The crystals are redissolved in 120 ml. of H_2O at 90°C, cooled to 0°C, suction-filtered, and dried in a desiccator. The yield is about 118 g. of 99.7% $AgClO_3$.

The compound should be stored in dark flasks. Since $AgClO_3$ is a strong oxidant, extreme care should be exercised when it is brought into contact with easily oxidized materials, especially organic substances.

PROPERTIES:

White crystals. M.p. 230°C, decomposes at 270°C; d 4.43.

DropBooks

REFERENCE:

D. G. Nicholson and C. E. Holley in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 4.

Silver Oxide

Ag_2O

$$\underset{339.8}{2\,AgNO_3} + \underset{80.0}{2\,NaOH} = \underset{231.8}{Ag_2O} + \underset{170.0}{2\,NaNO_3} + \underset{18.0}{H_2O}$$

Equivalent quantities of a conc. solution of $AgNO_3$ and a dilute solution of NaOH (both prepared with CO_2-free water) are mixed; the resultant precipitate is decanted and washed with CO_2-free water. The precipitate is centrifuged, suction-filtered, and dried at 85–88°C in a stream of CO_2-free air.

Alternate methods: a) Precipitation of a dilute $AgNO_3$ solution with $Ba(OH)_2$, with careful exclusion of CO_2 [E. Laue, Z. anorg. allg. Chem. 165, 336 (1927)].

b) Electrolytic preparation: A 25-30% $NaNO_3$ solution is electrolyzed at room temperature at minimum current density (anode current density is important), using a silver anode and a nickel cathode positioned as close as possible. [K. Merei, Magyar. Chem. Folyoirat 45, 197 (1913)].

PROPERTIES:

Dark brown to brown-black powder. M.p. (dec.) 300°C; d_4^{25} 7.220. Insoluble in water [solubility (20°C): $2.14 \cdot 10^{-3}$ g./100 g. H_2O]; somewhat soluble in NaOH. Moist Ag_2O is quite insensitive to light. Some decomposition occurs on drying. Crystal structure: type C3. Heat of formation (25°C): −7.3 kcal./mole.

REFERENCE:

E. H. Madsen. Z. anorg. allg. Chem. 79, 197 (1913).

Silver Peroxide

Ag_2O_2

Ag_2O	+ 2 KOH	+ 2 $KMnO_4$	= Ag_2O_2	+ 2 K_2MnO_4	+ H_2O
231.8	112.2	316.1	247.8	394.2	18.0

Solutions of $AgNO_3$ and $KMnO_4$ are combined and an excess of KOH is added. The resultant precipitate is filtered in a glass filtering crucible, washed with ice-cold water until the filtrate is colorless, dried for two hours at 110°C, and placed for 24 hours in a desiccator over P_2O_5. An anhydrous product containing up to 60% Ag_2O_2 is obtained.

Alternate methods: a) Treatment of $AgNO_3$ solution with a solution of potassium or ammonium persulfate [H. Marshall, J. Chem. Soc. (London) 59, 775 (1891)].

b) Reaction of metallic Ag with ozone-containing O_2 at 240°C; use of lower temperatures is also possible if Fe_2O_3 or Pt is used as catalyst [W. Manchot and W. Kampschulte, Ber. dtsch. chem. Ges. 40, 2891 (1907)].

c) Reaction of NaOCl with Ag_2O at 75-80°C [R. L. Dutta, J. Indian Chem. Soc. 32, 95 (1955)].

d) Hydrolysis of Ag_7NO_{11} (from anodic oxidation of $AgNO_3$ solutions) and thermal decomposition of Ag_7NO_{11} [G. M. Schwab and G. Hartmann, Z. anorg. allg. Chem. 281, 183 (1955)].

PROPERTIES:

Gray-black powder. Decomposes above 100°C into Ag and O_2; d_4^{25} 7.483. Soluble in conc. HNO_3, from which it precipitates

on dilution. Decomposes in hot conc. H_2SO_4 with evolution of O_2. Strongly oxidizing.

REFERENCE:

F. Jirsa. Z. anorg. allg. Chem. 225, 302 (1935).

Sodium Orthoargentite

Na_3AgO_2

$$\underset{231.8}{Ag_2O} + \underset{186.0}{3\,Na_2O} = \underset{417.7}{2\,Na_3AgO_2}$$

Stoichiometric quantities of pure, absolutely dry Na_2O and dry Ag_2O (dried in vacuum at 80°C) are weighed in the absence of moisture and CO_2. The two starting materials are ground to a fine powder and intimately mixed in the vacuum ball mill shown in Fig. 55, p. 76. The mixture is transferred (with exclusion of air) to a sintered magnesia boat placed in a protective tube of Fe or Ag which itself is positioned in a heating tube (Vycor or quartz). The heating tube is evacuated and the mixture heated to 400°C. The product is homogenized by grinding and reheating.

DropBooks

PROPERTIES:

Formula weight 208.85. Light green powder, highly sensitive to moisture. Decomposed to a black substance even by small quantities of water vapor. Stable up to 450°C in vacuum.

REFERENCE:

E. Zintl and W. Morawietz. Z. anorg. allg. Chem. 236, 372 (1938).

Silver (I) Sulfide

Ag_2S

$$\underset{215.8}{2\,Ag} + \underset{32.1}{S} = \underset{247.8}{Ag_2S}$$

I. Pure sulfur vapor, carried in a stream of N_2, is passed over pure Ag at 250°C. The S and Ag are in two separate boats placed in a quartz tube. Alternatively the S may be placed in a quartz

tube 18 cm. long and 16 mm. I.D. with a constriction in the middle (Fig. 278). That tube is open at one end and narrows to a conical nozzle at the other. The Ag is placed in a quartz tube, of the same diameter and about 9 cm. long, constricted at both ends in such a way that one of the ends fits the nozzle of the other tube. The other end is attached by means of a ground joint to an outlet tube for unreacted S vapor. The S, in a boat, is placed in the first of the two chambers formed by the 18-cm.-long quartz tube. Then the tubes containing the S and Ag are placed inside a larger quartz tube set in an electric furnace. The furnace is heated to 350°C in such a way that sulfur is distilled from the first into the second chamber of the 18-cm.-long tube (purification). The furnace is then set at 250°C and heating is continued in a stream of N_2.

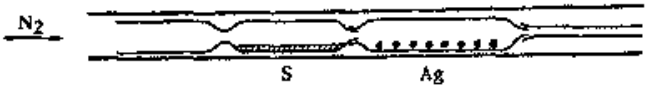

Fig. 278. Preparation of silver (I) sulfide.

Plugging of the outlet tube with excess S is prevented by heating the tube (if necessary, with an additional electric furnace). Depending on the flow rate, the conversion of 10 g. of Ag requires 6 to 8 hours. The excess S remaining in the Ag_2S after completion of the reaction is removed by heating in a stream of N_2. The temperature is maintained below 300°C to prevent sulfur from being driven off from the Ag_2S.

II. Very pure Ag and S are placed at opposite ends of an evacuated, sealed glass tube previously cleaned by the von Wartenberg method (p. 342). An excess of S is used. The tube is heated for 1-2 days at 400°C. It is then pulled (halfway) out of the furnace so that the end containing the sulfur is exposed on the outside. This enables the free sulfur to sublime from the product onto the cold excess sulfur. The reaction is complete within about 12 hours.

Alternate methods: a) Precipitation of an ammoniacal solution of $AgNO_3$ with H_2S. The precipitate is washed with water and dried at 150°C in a stream of CO_2. Excess S is removed by heating for one hour at 350-400°C in a stream of H_2 [E. von Britzke and A. F. Kapustinski, Z. anorg. allg. Chem. 205, 95 (1932)].

b) Fusion of the calculated amounts of Ag and S in a pressure vessel [A. M. Gaudin and D. W. McGlashan, Econ. Geol. 33, 143 (1932)].

SYNONYM:

Argentous sulfide.

PROPERTIES:

Black, crystalline. M.p. 845°C; d_4^{20} 7.234, $d_4^{17.8-4}$ 7.072. Soluble in KCN solution, insoluble in aqueous ammonia. Transition point β-Ag_2S (rhombic) → α-Ag_2S (cubic): 179°C. Heat of formation (α-Ag_2S, 25°C): −7.5 kcal./mole.

REFERENCES:

I. O. Hönigschmid and R. Sachtleben, Z. anorg. allg. Chem. 195, 207 (1931).
II. C. Wagner, Private communication.

Silver (I) Selenide

Ag_2Se

$$2\,Ag + Se = Ag_2Se$$
$$215.8 \quad 79.0 \quad 294.7$$

A boat containing selenium and (behind it) a boat containing metallic silver are placed inside a quartz tube. The tube is surrounded by two electrical furnaces, so that the Se is heated to 300°C, while the Ag is at 400°C. A stream of O_2-free nitrogen carries the Se to the silver (see Fig. 278, preparation of Ag_2S). The Se vapor is passed over the metal until large amounts of Se begin to accumulate behind the Ag. The heat is maintained at 400°C for some time after that to remove any Se which may have adhered to the product surface. The conversion of 5 g. of Ag requires 6-8 hours. Dissociation begins above 400°C.

Alternate method: Reaction of soluble Ag salts with CuSe. The reactions with Cu_2Se and Cu_3Se_2 give metallic Ag as a by-product [W. Geilmann and Fr. W. Wrigge, Z. anorg. allg. Chem. 210, 378 (1933)].

PROPERTIES:

Black, crystalline. d_4^{24} 8.187. Crystal structure: at 75°C tetragonal with $c/a = 0.66$; at 80°C tetragonal with $c/a = 0.94$; at 240°C cubic. Heat of formation (cubic Ag_2Se, 25°C): −5.0 kcal. per mole.

REFERENCE:

O. Hönigschmid and W. Kapfenberger, Z. anorg. allg. Chem. 212, 198 (1933).

Dropbooks

Silver (I) Telluride

Ag_2Te

$$2\,Ag + Te = Ag_2Te$$
$$215.8 \quad 127.6 \quad 343.4$$

Prepared by passing Te vapor over Ag. Nitrogen serves as the carrier gas and the reaction temperature is 470°C. The flow rate of the Te vapor should be slow; i.e., the amount of Te entering the reaction chamber should not exceed the reactive capacity of the Ag. The apparatus is identical to that used for Ag_2Se. The conversion of 3 g. of Ag requires 72-96 hours. Excess Te is removed by heating to 500-540°C in high vacuum. Well-crystallized products are obtained.

Alternate method: Heating Ag in a porcelain crucible in an atmosphere of Te, with exclusion of air [P. Rahlfs, Z. phys. Chem. (B) 31, 157 (1936)].

PROPERTIES:

Gray-black, crystalline. d_4^{20} 8.318. Transition point β-Ag_2Te (rhombic) $\rightarrow$ α-Ag_2Te (cubic): 149.5°C. Heat of formation (β-Ag_2Te, 25°C) −5.0 kcal./mole.

REFERENCE:

O. Hönigschmid, Z. anorg. allg. Chem. 214, 281 (1933).

Silver Sulfate

Ag_2SO_4

$$2\,AgNO_3 + H_2SO_4 = Ag_2SO_4 + 2\,HNO_3$$
$$339.8 \quad 98.1 \quad 311.8 \quad 126.0$$

A solution of $AgNO_3$ in some H_2O is treated with 1:1 sulfuric acid. The Ag_2SO_4 precipitate is centrifuged, dissolved in hot conc. H_2SO_4 (in a Pt dish if high product purity is required), and boiled for several minutes to expel the nitric acid. The acid sulfate which crystallizes on cooling is centrifuged and treated with water in a Pt dish. The normal sulfate thus crystallizes as a fine powder (evolution of heat). The supernatant is decanted and the crystals washed with pure water until free of acid. The Ag_2SO_4 is centrifuged and dried on an air bath at 110°C. The entire operation must be conducted in a dustproof atmosphere.

Alternate methods: a) Treatment of $AgNO_3$ solution with Na_2SO_4 solution [O. Hönigschmid and R. Sachtleben, Z. anorg. allg. Chem. 195, 207 (1931)].

b) Solution of Ag metal in sulfuric acid (O. Hönigschmid and R. Sachtleben, loc. cit.).

c) Finely divided Ag_2SO_4 is obtained by precipitation of its aqueous solution with alcohol. The product is dried in vacuum at 100°C [H. Hahn and E. Gilbert, Z. anorg. allg. Chem. 258, 91 (1949)].

PROPERTIES:

Colorless crystals. M.p. 657°C, decomposes at 1085°C; d_4^{15} 5.460. Sparingly soluble in water; solubility (18°C): $2.57 \cdot 10^{-2}$ g./100 g. H_2O. Slightly decomposed by light, acquiring a light-violet color. Dissociates on melting, acquiring a yellow color which disappears on treatment with gaseous SO_3. Crystal structure: orthorhombic. Heat of formation (25°C): −170.5 kcal./mole.

REFERENCE:

Th. W. Richards and G. Jones, Z. anorg. allg. Chem. 55, 72 (1907).

Silver Sulfite

Ag_2SO_3

$$\underset{339.8}{2\,AgNO_3} + \underset{126.0}{Na_2SO_3} = \underset{295.8}{Ag_2SO_3} + \underset{170.0}{2\,NaNO_3}$$

A solution of $AgNO_3$ is treated at room temperature with the stoichiometric quantity of Na_2SO_3 solution, yielding a precipitate of Ag_2SO_3, which is filtered, washed with well-boiled water, and dried in vacuum.

Alternate method: Precipitation of aqueous $AgNO_3$ with sulfurous acid [J. Muspratt, Liebigs Ann. 50, 286 (1853)].

PROPERTIES:

Colorless powder. Sparingly soluble in water, soluble in aqueous ammonia. Decomposes in light and on heating, forming the dithionate and sulfate. Insoluble in liquid SO_2.

REFERENCES:

P. Berthier, Ann. Chim. Phys. (3) 7, 82 (1817); K. Seubert and M. Elten, Z. anorg. allg. Chem. 4, 44 (1894).

Silver Amide

$AgNH_2$

$$\underset{169.9}{AgNO_3} + \underset{55.1}{KNH_2} = \underset{123.9}{AgNH_2} + \underset{101.1}{KNO_3}$$

Silver amide is formed in the reaction between potassium amide and silver nitrate, both dissolved in liquid ammonia. Good

results are obtained with the two-arm tube shown in Fig. 279, in which KNH_2 solution is allowed to flow into excess $AgNO_3$ solution, causing precipitation of $AgNH_2$.

A) KNH_2

First, KNH_2 is prepared in arm B from potassium metal and NH_3. To achieve this, inlet tube c is connected to a source of absolutely dry NH_3 and the entire apparatus is dried by passing through NH_3 and heating. Then a is temporarily closed off with a stopper and oxide-free K, together with a few milligrams of sponge Pt as catalyst, is introduced at b in a stream of NH_3. Inlet tube b is melt-sealed to a pressure-resistant tip, the pressure gradient required for the glass-blowing operation being achieved by brief alternate closing and opening of inlet a with a finger. The $AgNO_3$ is now introduced into arm A and dried in a stream of NH_3. Arm A is then melt-sealed at a in the same way as b, the pressure gradient being achieved by removing the plug from stopcock h and closing the resultant two openings (when required) with a finger. Arm B is then immersed in ice water and NH_3 is allowed to condense in it until it fills 1/4 of the volume. In the presence of Pt, 1 g. of K is converted to KNH_2 within 15 minutes. After completion of the reaction, the H_2 by-product is allowed to escape via stopcock h.

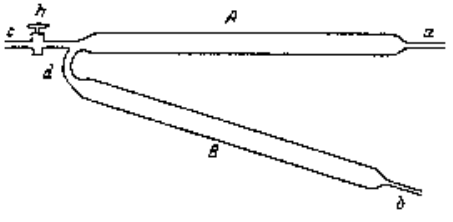

Fig. 279. Preparation of silver amide.

B) $AgNH_2$

The $AgNO_3$ in arm A is dissolved in a manner similar to that presented above, and both arms are then filled to half their volume with liquid NH_3. After the solutions have become homogeneous, they are combined by allowing the KNH_2 solution to flow into the $AgNO_3$ solution. The resultant precipitate of $AgNH_2$ settles well and is purified by decantation with liquid NH_3. This is carried out by pouring the supernatant liquid NH_3 into arm B and redistilling it into A (B is then in lukewarm water, A in ice water). The precipitate is vigorously agitated, together with the NH_3 which condenses on it, and is then allowed to settle. The

supernatant liquid NH_3 is again poured off into *B*. This operation is repeated several times. Finally a deep layer of liquid NH_3 is condensed onto the precipitate in *A*. This arm is then immersed in a −35°C bath in order to establish atmospheric pressure inside the apparatus, stopcock *h* is opened, and the tube is fused at *d*. The liquid NH_3 is allowed to evaporate slowly through stopcock *h* and the tube is evacuated to remove residual NH_3.

These reactions may also very conveniently be carried out in the apparatus of Fig. 69, p. 87; this apparatus is an improved version of the one described above.

PROPERTIES:

White, quite voluminous precipitate (when moist). Soluble in ammonium salt solutions, absolute ammonia, and excess KNH_2; insoluble in excess $AgNO_3$. Blackens on exposure to light. The precipitate shrinks considerably on drying and acquires color. Extraordinarily explosive when dry. Apparently impossible to obtain an absolutely pure state.

REFERENCES:

E. C. Franklin. Z. anorg. allg. Chem. 46, 1 (1905); R. Juza. Z. anorg. allg. Chem. 231, 121 (1937).

DropBooks

Silver Azide

AgN_3

$$\underset{169.9}{AgNO_3} + \underset{65.0}{NaN_3} = \underset{149.9}{AgN_3} + \underset{85.0}{NaNO_3}$$

A solution of NaN_3 is treated in the cold with a slight excess of $AgNO_3$ solution. The AgN_3 precipitate is decanted, filtered, washed with water, alcohol and ether, and dried in vacuum over conc. H_2SO_4.

Alternate methods: a) Slow addition of a 1% $AgNO_3$ solution to 1.5% aqueous HN_3, prepared by distillation of a solution of NaN_3 in H_2SO_4. The product is washed free of Ag ion [F. V. Friedländer, J. Amer. Chem. Soc. 40, 1945 (1918); T. Curtius, Ber. dtsch. chem. Ges. 23, 3027 (1890)].

b) Precipitation of a cold, saturated solution of $AgNO_3$ with hydrazine sulfate [A. Angeli, Atti Acad. dei Linc. 2, 569 (1893)].

PROPERTIES:

Colorless crystalline needles. M.p. 252°C. Sparingly soluble in water and nitric acid; readily soluble in aqueous ammonia

Highly explosive. Sensitive to shock and heat. The white color changes to gray-violet on heating to 170–180°C. Detonation temperature about 300°C. Crystal structure: orthorhombic. Heat of formation: +67.3 kcal./mole.

REFERENCE:

G. Tammann and C. Kröger. Z. anorg. allg. Chem. 169, 16 (1928).

Silver Nitride

Ag_3N

Potassium hydroxide pellets are added to a solution of AgCl in conc. ammonia until the effervescence, caused by the evolving NH_3, stops. The mixture is diluted with distilled water, filtered through filter paper, and washed with water until the filtrate is neutral. The moist product is transferred from the filter paper to a porcelain dish, where it may be stored under water for some time.

The product contains small amounts of AgCl and Ag, but is free of Ag_2O.

Alternate methods: a) A solution of Ag_2O in conc. aqueous ammonia is allowed to stand in air or heated on a water bath. The same may be achieved by precipitation with alcohol. The product is impure, with a variable content of Ag_2O and Ag [F. Raschig, Liebigs Ann. 233, 93 (1886)].

b) Solid $AgF \cdot 2NH_3$ is stored for several days over H_2SO_4 in a desiccator. The product is free of Ag_2O and rich in Ag; the yield is small [L. J. Olmer and Dervin, Bull. Soc. Chim. France (4) 35, 152 (1924)].

SYNONYM:

(Berthollet's) fulminating or detonating silver.

PROPERTIES:

Formula weight 337.65. Black flakes, sometimes shining black; crystalline appearance (when prepared according to Raschig, see above). Insoluble in H_2O, soluble in dilute mineral acids, explosive reaction with conc. acids. Both the dry and the moist product may be stored in air at room temperature for a long time. Slowly decomposes at 25°C. Decomposes at room temperature in vacuum. Decomposes explosively in air at about 165°C. Very sensitive

(explodes) when touched with objects of great relative hardness, even when moist. Extremely sensitive when dry, but relatively easy to handle when moist. Explodes readily when prepared by Raschig's method. d_4^{18} 9.0. Crystal structure: cubic. Heat of formation (25°C): +61.0 kcal./mole.

REFERENCE:

H. Hahn and E. Gilbert. Z. anorg. Chem. 258, 77 (1949).

Silver Acetylide

Ag_2C_2

$$\underset{339.8}{2\,AgNO_3} + \underset{22.41.}{C_2H_2} = \underset{239.8}{Ag_2C_2} + \underset{126.0}{2\,HNO_3}$$

Pure acetylene is introduced into a solution of $AgNO_3$ which has been treated with a large excess of ammonia. The white precipitate of Ag_2C_2 is filtered, washed with water, then with alcohol and ether, and dried over P_2O_5 in a desiccator.

PROPERTIES:

White powder, light sensitive, very explosive, particularly when dry. Soluble (decomposition) in KCN solution, yielding C_2H_2. Decomposed by HCl into AgCl and C_2H_2. Decomposes hydrolytically in water and alkalis.

PrepBooks

REFERENCE:

J. Eggert. Z. Elektrochem. 24, 150 (1918).

Silver Cyanamide

Ag_2CN_2

Careful addition of HNO_3 to commercial $CaCN_2$ at 0°C and pH 6 yields H_2CN_2. The solution thus obtained, which contains about 10% H_2CN_2, is treated with an ammoniacal solution of $AgNO_3$ (added in small portions). The resultant Ag_2CN_2 is purified by solution in dilute HNO_3 and reprecipitation with dilute NH_3; it is washed and rapidly dried at 130°C.

PROPERTIES:

Formula weight 255.79. Yellowish-white powder containing 99.5% Ag_2CN_2. Soluble in KCN: $Ag_2CN_2 + 4\,KCN = 2K[Ag(CN)_2] + K_2CN_2$. Pyrolysis in vacuum proceeds via the intermediate

silver dicyanamide, AgC_2N_3, which is stable up to 600°C. The decomposition is complete at 750°C. The residue consists of Ag which is free of cyanide and N_2. If the temperature rise is too rapid, the pyrolysis becomes explosive.

REFERENCE:

A. Chrétien and B. Woringer. Compt. Rend. Hebd. Séances Acad. Sci. 232, 1114 (1951).

Silver Carbonate

Ag_2CO_3

$$\underset{339.8}{2\,AgNO_3} + \underset{106.0}{Na_2CO_3} = \underset{275.8}{Ag_2CO_3} + \underset{170.0}{2\,NaNO_3}$$

A solution of $AgNO_3$ is treated with alkali carbonate or bicarbonate. When precipitating with the carbonate, avoid an excess of the reagent, since the Ag_2CO_3 precipitate may then contain oxides. The product is filtered, washed with water, and dried to constant weight over H_2SO_4 and P_2O_5. It still contains traces of water.

Due to its sensitivity to light, a pure silver carbonate can be obtained only when the preparation is carried out in red light.

Alternate method: Electrolysis of a 0.02M solution of $NaHCO_3$ using a silver anode and platinum cathode. The crystalline precipitate at the anode is Ag_2CO_3 [P. Demers, Canad. J. Res. (A) 17, 77 (1939)].

PROPERTIES:

Light-yellow powder. Very sparingly soluble in water; solubility (25°C): $3.2 \cdot 10^{-3}$ g./100 g. H_2O. Soluble in conc. alkali carbonate solutions, KCN solution, HNO_3 and H_2SO_4. Splits off CO_2 on heating (CO_2 pressure at 218°C = 752 mm.). d_4^{20} 6.077. Heat of formation (25°C): −120.8 kcal./mole.

REFERENCE:

G. H. G. Jeffrey and A. W. Warnington. Chem. News 132, 373 (1939).

Silver Nitrite

$AgNO_2$

$$\underset{169.9}{AgNO_3} + \underset{85.1}{KNO_2} = \underset{153.9}{AgNO_2} + \underset{101.1}{KNO_3}$$

A solution of 5 parts of KNO_2 is added to a solution of 8 parts of $AgNO_3$. The resultant pale yellow precipitate is usually

contaminated with some Ag_2O, which is removed by recrystallization from water at 70°C. On cooling, $AgNO_2$ crystallizes in the form of hair-thin, almost colorless needles. It is best to work under red light to prevent decomposition.

PROPERTIES:

Colorless to yellow needles. Somewhat soluble in water; the solubility increases markedly with temperature: (15°C) 0.28, (60°C) 1.38 g./100 g. H_2O. Soluble in excess nitrites, with formation of complex salts. Blackens in light. Decomposes at 140°C; dissociates into Ag and NO_2 on dry heating. In aqueous solution, gradually decomposes into Ag, $AgNO_3$ and NO. d_4^{26} 4.453. Crystal structure: orthorhombic. Heat of formation: —11.6 kcal./mole.

REFERENCE:

J. A. A. Ketelaar. Z. Kristallogr. (A) 95, 383 (1936).

Silver Tartrate

$Ag_2C_4H_4O_6$

$$2\,AgNO_3 + KNaC_4H_4O_6 \cdot (4\,H_2O) = Ag_2C_4H_4O_6 + KNO_3 + NaNO_3$$

339.8 282.2 363.8 101.1 85.0

DropBooks

Stoichiometric quantities of $AgNO_3$ and potassium sodium tartrate (Rochelle salt) are dissolved in water and the solutions combined. On addition of alcohol (in which silver tartrate is insoluble), the product precipitates as a white, cheeselike deposit which is immediately filtered through a suction or Büchner filter. The precipitate is washed with aqueous alcohol until no further Ag^+ ion is detectable. Further purification may be achieved by crystallization from 80°C water, a small quantity of Ag_2O being formed in the process. The aqueous solution is filtered and alcohol is again added. The precipitate is filtered, washed first with aqueous, then with absolute alcohol or acetone, and dried in vacuum over H_2SO_4.

Due to the light sensitivity of the compound, it is best to work in the dark.

Alternate method: A hot, moderately conc. solution of Rochelle salt is added to an 80°C dilute solution of $AgNO_3$; the reaction (addition) is complete when the continually forming precipitate no longer dissolves. The silver tartrate crystallizes on cooling in the form of fine flakes which acquire a white, metallic sheen on washing.

PROPERTIES:

White powder or crystalline flakes, not entirely stable in daylight. Soluble in dilute nitric acid, sparingly soluble in H_2O (solubility at 25°C: 0.20 g./100 g. H_2O); insoluble in alcohol, acetone and ether. Decomposes in ammonia and NaOH, yielding Ag_2O. Evolves CO_2 on dry heating, leaving pyrotartaric acid and Ag as residue. d_4^{15} 3.432.

REFERENCES:

L. Redtenbacher. Liebigs Ann. 38, 132 (1841); H. Sauer. Unpublished.

o-Phenanthrolinesilver (II) Persulfate

$[Ag\,phen_2]S_2O_8$

$$\underset{339.8}{2\,AgNO_3} + \underset{720.8}{4\,C_{12}H_8N_2} + \underset{684.6}{3\,(NH_4)_2S_2O_8} = \underset{1320.9}{2\,[Ag(C_{12}H_8N_2)_2]S_2O_8} + \underset{264.3}{2\,(NH_4)_2SO_4} + \underset{160.1}{2\,NH_4NO_3}$$

Two equivalents of an aqueous solution of o-phenanthroline are added to a solution of $AgNO_3$. A colorless, gelatinous precipitate is formed; it rapidly turns red-brown on addition of a conc. solution of $(NH_4)_2S_2O_8$, and settles on standing as fine crystals. The product is suction-filtered, washed with cold water, and dried, first with alcohol and ether and then in a desiccator. The yield is quantitative.

PROPERTIES:

Formula weight 660.44. Chocolate brown, very stable crystalline powder. Insoluble in water. Readily soluble (without decomposition) in cold conc. nitric acid, yielding a dark brown solution from which the perchlorate may be precipitated by addition of an excess of conc. $NaClO_4$ solution. Forms AgO in alkali hydroxides.

REFERENCE:

W. Hieber. Ber. dtsch. chem. Ges. 61, 2149 (1928).

Tris-α,α'-dipyridylsilver (II) Perchlorate

$[Ag(dipyr)_3](ClO_4)_2$

The reaction between silver nitrate and α,α'-dipyridyl yields bis-α,α'-dipyridylsilver nitrate $[Ag(dipyr)_2]NO_3$, which is converted into bis-α,α'-dipyridylsilver(II) persulfate $[Ag(dipyr)_2]S_2O_8$

with $K_2S_2O_8$. Treatment of this compound with nitric acid yields tris-α,α'-dipyridylsilver (II) nitrate $[Ag(dipyr)_3](NO_3)_2$; addition of $NaClO_4$ to an aqueous solution of this nitrate yields a precipitate of the corresponding perchlorate.

A) BIS-α,α'-DIPYRIDYLSILVER NITRATE $[Ag(dipyr)_2]NO_3$

A hot solution of 16.9 g. of $AgNO_3$ in aqueous ethanol is added to a hot solution of 31.2 g. of α,α'-dipyridyl in ethanol, yielding a precipitate of $[Ag(dipyr)_2]NO_3$. Additional product is recovered upon concentration of the mother liquor. The compound is recrystallized from hot dilute ethanol.

PROPERTIES:

Formula weight 482.27. Yellow needles. Decomposes at 155°C. Decomposes slowly in light. Sparingly soluble in cold and hot water and in common organic solvents (except alcohols).

B) BIS-α,α'-DIPYRIDYLSILVER (II) PERSULFATE $[Ag(dipyr)_2]S_2O_8$

The yellow needles of $[Ag(dipyr)_2]NO_3$ are stirred into an excess of cold, saturated aqueous $K_2S_2O_8$; a deep red-brown precipitate of the complex persulfate is produced. The reaction is complete after two hours of constant stirring. The precipitate is washed with cold water.

DropBooks

PROPERTIES:

Formula weight 612.39. Red-brown precipitate. Decomposes at 137°C. Very sparingly soluble in water, insoluble in the common organic solvents. In air, converts to the corresponding hydrogen sulfate.

C) TRIS-α,α'-DIPYRIDYLSILVER (II) NITRATE $[Ag(dipyr)_3](NO_3)_2$

Product (B) is triturated in a mortar with cold nitric acid (d 1.4). The excess acid is removed and the residue extracted with warm water. The brown aqueous extract is treated with an excess of aqueous NH_4NO_3 and cooled with ice, thus precipitating small, dark-brown needles of the dinitrate. The precipitate is purified by solution in warm water and reprecipitation with aqueous NH_4NO_3.

PROPERTIES:

Formula weight 700.47. Dark-brown needles. Decomposes at 176°C. Soluble in water; the aqueous solution decomposes slowly, evolving O_2. Powerful oxidant.

D) TRIS-α,α'-DIPYRIDYLSILVER (II) PERCHLORATE $[Ag(dipyr)_3](ClO_4)_2$

This compound is precipitated when $NaClO_4$ is added to an aqueous solution of $[Ag(dipyr)_3](NO_3)_2$. The precipitate is washed with warm water.

PROPERTIES:

Formula weight 775.36. Orange-brown crystals. Detonates on heating. Very sparingly soluble in water.

ANALYSIS:

Determination of the Ag (II) in compounds B–D: the complex salts are treated with cold aqueous KI, yielding iodine: $AgX_2 + 2\ KI \rightarrow 2\ KX + AgI + {}^1/_2\ I_2$. The iodine is titrated with $Na_2S_2O_3$ solution.

REFERENCES:

G. T. Morgan and F. H. Burstall. J. Chem. Soc. (London) 1930, 2594; H. Kainer. Thesis, Heidelberg, 1952.

Very Pure Gold

Gold (20 g.) is dissolved in aqua regia in an 800-ml. beaker, and the solution is concentrated to a thick sirup. The nitric acid is expelled by evaporating the solution five times on a steam bath, each time with 20 ml. of hydrochloric acid (4:1). The residue is taken up in 650 ml. of hot water and digested until all soluble material is dissolved. It is then allowed to settle for eight days in a dust-free atmosphere. The precipitate consists of AgCl containing small amounts of Au, Pd, SiO_2, etc. The gold solution is filtered through a double layer of thick filter paper, without disturbing the precipitate. This and all later precipitates are not worked up further to obtain gold.

Experience indicates that the gold refined by use of SO_2 still contains some Pd, while that precipitated with oxalic acid contains Cu, Pb and other metals. Therefore both of these procedures must be used to obtain gold of the desired purity. Sulfur dioxide is passed through the warm gold solution (80°C) obtained above; the gold precipitates quantitatively on careful neutralization with ammonia (1:1). The product is allowed to settle overnight and the deposit of spongy gold is washed by decantation with hot water; it is then heated for four hours on a steam bath with conc. hydrochloric acid and washed free of acid with hot water. Then it is redissolved

in a beaker. The entire procedure is repeated eight times in order to remove Ag, Cu, Ni, Zn and Pb. The product is then digested for 12 hours with ammonia (1:1), washed free of ammonia with water, heated for four hours on a steam bath with hot conc. nitric acid, and decanted. Ammonia (1:1) is again added and later removed by washing with water. The gold sponge is dissolved in dilute aqua regia; after addition of HCl, the solution is concentrated by evaporation, diluted with H_2O, decanted and filtered. The gold is precipitated by careful addition (there is a danger of foaming over) of small portions of powdered, crystalline oxalic acid. If the solution retains a yellow color, it is carefully neutralized with ammonia and more oxalic acid is added; the addition of the acid is continued until the solution remains colorless. The resultant gold sponge is dissolved and reprecipitated with oxalic acid. It is then Pd-free. Finally the gold is redissolved, precipitated with SO_2, digested with conc. hydrochloric acid, and washed with water. The last traces of HCl are removed with ammonia. The product is transferred to a glazed porcelain dish and dried at 110°C. Yield 75–80%. The gold prepared in this manner is spectroscopically pure (free of metallic Cu, Ag, Ni, Zn and Pt).

Alternate methods: a) Preparation of pure gold by the method of G. Krüss. The product is probably not as pure as that prepared by the method described above [G. Krüss, Liebigs Ann. 238, 43 (1887)].

b) Extraction of $AuCl_3$ with ether. Total impurities in the product, about 0.001% [F. Mylius, Z. anorg. allg. Chem. 70, 203 (1911)].

DTODBOOKS

PROPERTIES:

Atomic weight 197.0. M.p. 1063°C, b.p. 2960°C; $d_4^{17.5}$ 19.29. Crystal structure: type A1.

REFERENCE:

T. A. Wright. Metals and Alloys 3, 146 (1932).

Colloidal Gold

A mixture of 120 ml. of very pure, twice-distilled water (silver condenser) and 2.5 ml. of a solution of 6 g. of $HAuCl_4 \cdot 4\,H_2O$ in one liter of water is prepared and brought to a boil as rapidly as possible. Shortly before the boiling point is reached, 3 ml. of 0.18N solution of very pure potassium carbonate is added. As soon as the solution begins to boil, it is rapidly swirled around

(or stirred with a Pyrex glass rod), while 3-5 ml. of a dilute solution of formaldehyde (1.3 ml. of 40% formaldehyde in 100 ml. of water) is added. Stirring is continued until a reaction is evident (this usually occurs within a few seconds—one minute at most), whereupon the solution becomes bright red. It is again brought to a boil and held at the b.p. for a short time until the odor of formaldehyde disappears.

Alternate methods: a) Reduction with ethereal solution of phosphorus (R. Zsigmondy and P. A. Thiessen, Das kolloide Gold [Colloidal Gold], Leipzig, 1925, p. 487).

b) Reduction with hydrazine hydrate or phenylhydrazonium chloride [A. Gutbier and F. Resenscheck, Z. anorg. allg. Chem. 39, 112 (1904)].

c) Reduction with sodium anhydro methylene citrate (citramin) [L. Vanino, Kolloid-Z. 20, 122 (1917)].

d) Reduction with alkaline formaldehyde solution [P. P. von Weimarn, Kolloid-Z. 33, 75 (1923)].

e) Sol of gold by pulverization in an electric arc [Th. Svedberg, Ber. dtsch. chem. Ges. 39, 1705 (1906); G. Bredig, Angew. Chem. 950 (1898); E. F. Burton, Phil. Mag. 11, 425 (1906)].

PROPERTIES:

Bright red sol, particle size about $1\text{-}6 \cdot 10^{-7}$ cm. Highly sensitive to electrolytes. Concentrated solutions (up to 0.12% gold) may be obtained by dialysis.

REFERENCE:

R. Zsigmody and P. A. Thiessen. Das kolloide Gold [Colloidal Gold], Leipzig, 1925, p. 33.

Gold from Residues

I. FROM PLATING BATHS

A clay cell filled with NaCl solution and provided with a zinc electrode is placed in the gold solution. An electrode made of a piece of brass sheet is immersed in the gold solution and the two electrodes are connected into a circuit. The gold is deposited quantitatively on the brass electrode over a period of a few weeks, during which the brass electrode is replaced once or twice and the Zn electrode is pickled several times.

II. FROM WASTE CONTAINING GOLD AND SILVER

The particles are calcined and the resultant powder is boiled with conc. nitric acid to remove Ag and other metals. The diluted

solution is filtered and the residue is heated with aqua regia on a steam bath for 24 hours. The gold is precipitated from the filtrate with $FeSO_4$ and worked up.

III. FROM INDUSTRIAL ALLOYS

The gold alloy is ground as finely as possible and heated with conc. hydrochloric acid on a sand bath, conc. nitric acid being added in drops from time to time. When solution is complete, the mixture is evaporated in a porcelain dish placed on a steam bath (dust-free atmosphere) until the liquid solidifies on cooling. The residue is taken up in a large quantity of water and allowed to stand for some time; the precipitated AgCl is then filtered off. The solution is heated and the gold is precipitated with excess aqueous $FeCl_2$. The supernatant is decanted and the residue boiled with dilute hydrochloric acid until the HCl ceases to yellow. The solution is then filtered, dried and fused with borax in a porcelain crucible. If higher purity is desired, the procedure is repeated. If present, Pt, Pd and Tl may be removed from the filtrate with Fe or Zn.

Alternate methods: a) Reduction with alkaline H_2O_2 [L. Vanino and L. Seemann, Ber. dtsch. chem. Ges. 32, 1968 (1899)].

b) The gold solution is added at 100°C to a solution of $Hg_2(NO_3)_2$, yielding very finely divided gold (L. Vanino, Handbuch der präp. Chemie [Handbook of Prep. Chemistry], Stuttgart, 1921, Vol. I, p. 520).

c) Electrolysis of Ag- and Pt-containing alloys [W. Möbius, Berg- und hüttenm. Ztg. 44, 447 (1885); 47, 324 (1888); Chemiker-Ztg. 15, Rep. 18 (1891); E. Wohlwill, Z. Elektrochem. 4, 379 (1897)].

DropBooks

REFERENCES:

I. Plage, Industr.-Bl. 190 (1878).
II. W. Adolphi, Chemiker-Ztg. 52, 109 (1928).
III. A. Bender, Anleitung z. Darstellung anorg. Präparate [Introduction to the Preparation of Inorganic Compounds], Stuttgart, 1893.

Gold (I) Chloride

AuCl

Prepared by thermal decomposition of an auric chloride obtained from hydrogen tetrachloroaurate (III).

$$\underset{(4\,H_2O)}{HAuCl_4} = AuCl + HCl + Cl_2$$

411.9 232.5 36.5 70.9

Gold (5–10 g.) is dissolved in aqua regia and the solvents are removed by vacuum distillation (aspirator) at water bath temperature.

The solution is protected by a blanket of CO_2 introduced through a capillary. The nitric acid is expelled by double evaporation with conc. hydrochloric acid, and the resultant dark red-brown melt is poured into a dish where it congeals to a crystalline mass. This is heated to 100°C in high vacuum, until no vapor pressure is evident. Since the $HAuCl_4$ liquefies again during this operation, care should be exercised to avoid spattering. After all water is expelled, the residue is heated to 156°C (boiling bromobenzene bath). At higher temperatures (170–205°C) the decomposition is complete within a few hours.

Alternate methods: a) Thermal decomposition of $AuCl_3$ in air at 185°C [J. Thomsen, J. prakt. Chem. 13, 337 (1876)].

b) Decomposition of $AuCl_3$ in a stream of dry HCl at 175°C [M. E. Diemer, J. Amer. Chem. Soc. 35, 552 (1913)].

c) Decomposition of $AuCl_3$ in a stream of dry air [F. H. Campbell, Chem. News 96, 17 (1907)].

The products prepared by methods a-c are not completely pure.

SYNONYMS:

Aurous chloride, gold monochloride.

PROPERTIES:

Light yellow crystals, not deliquescent. M.p. (dec.) 289°C; d_4^{25} 7.4. Soluble in alkali chloride solutions. Decomposes on solution in water. Heat of formation (25°C): −8.4 kcal./mole.

REFERENCE:

W. Biltz and W. Wein. Z. anorg. allg. Chem. 148, 192 (1925).

Gold (III) Chloride

$AuCl_3$

I.

$$\underset{394.0}{2\,Au} + \underset{67.21.}{3\,Cl_2} = \underset{606.7}{2\,AuCl_3}$$

Finely divided gold is treated at 225–250°C (but not higher) with gaseous Cl_2 at a pressure of 900–950 mm. (The gold powder is obtained by precipitating a solution of a gold salt with sulfurous acid, washing and drying at 180°C.) The powder is in a porcelain boat which is placed in a glass tube. At the point immediately adjoining the boat, the tube widens into a sphere with outlets at

top and bottom. Excess Cl_2 escapes through the upper outlet; this outlet also carries a rod, which can be used to push the $AuCl_3$ (which condenses in the sphere) into a storage flask via the lower outlet. The yield is 0.1–0.2 g. per hour of large (up to 10 mm. long) crystals.

II. About 0.2–0.6 g. of freshly precipitated gold is placed in a 50-ml. flask connected to the atmosphere via a reflux condenser and a drying tower. Molten iodine monochloride is added in drops through a side tube. The reaction starts when the flask is heated. When the reaction subsides, an excess of ICl is added and the mixture is heated for a short time until boiling just begins. The solution is cooled and extracted several times with CCl_4 (distilled over P_2O_5). The suspension is then filtered (suction) in a stream of N_2 through a sintered glass funnel; the residue is washed with CCl_4 and freed of CCl_4 in vacuum. The yield is quantitative.

Alternate method: $HAuCl_4 \cdot 4\,H_2O$ is carefully heated in a stream of Cl_2; final heating for half an hour at 200°C [M. E. Diemer, J. Amer. Chem. Soc. 35, 553 (1913)].

SYNONYMS:

Auric chloride, gold trichloride.

REFERENCES:

Formula weight 303.37. Ruby-red crystals (when sublimed) or red-brown to dark ruby-red crystalline mass. M.p. 229°C, b.p. (dec.) 254°C; d_4^{20} 3.9. Melts at 288°C under a Cl_2 pressure of 2 atm. Sublimes at 180°C. Hygroscopic; soluble in H_2O with formation of $H_2[AuCl_3O]$. The neutral aqueous solution decomposes gradually with separation of metallic gold; acidic solutions are more stable. Soluble in alcohol and ether. Heat of formation (25°C): −28.3 kcal./mole.

REFERENCES:

I. M. Petit, Bull. Soc. Chim. France, Mém. 37/38, 1141 (1925); W. Fischer and W. Biltz, Z. anorg. allg. Chem. 176, 81 (1928).
II. V. Gutmann, Z. anorg. allg. Chem. 264, 169 (1951).

Hydrogen Tetrachloroaurate (III)

$HAuCl_4 \cdot 4\,H_2O$

$$2\,Au + 3\,Cl_2 + 2\,HCl = 2\,HAuCl_4 \cdot (4\,H_2O)$$

394.0 212.7 72.9 823.8

Precipitated gold is dissolved in aqua regia and the solvent is evaporated at steam bath temperature (aspirated vapor). The nitric

acid is expelled by repeating the procedure twice with conc. hydrochloric acid, which is itself removed by evaporation. The resultant melt is poured into a dish, where it congeals to a crystalline mass. The residual mother liquor is decanted, and the crystals are crushed to allow rapid drying in a drying closet. The mass is pulverized several times during the drying operation until it is completely dry.

PROPERTIES:

Formula weight 411.90. Elongated, light-yellow needles, deliquescent in moist air. Soluble in water, alcohol and ether. The anhydrous compound crystallizes from alcohol. One molecule of H_2O is given off on prolonged standing in dry air. Crystal structure: monoclinic. Heat of formation: −4.5 kcal./mole.

SYNONYMS:

Gold trichloride acid; chloroauric acid; aurochlorohydric acid; hydrochloroauric acid.

REFERENCES:

W. Biltz and W. Wein. Z. anorg. allg. Chem. 148, 192 (1925); J. Thomsen. Ber. dtsch. chem. Ges. 16, 1585 (1883).

Potassium Tetrachloroaurate (III)

$$KAuCl_4 \cdot {}^1/_2\, H_2O$$

$$\underset{606.7}{2\,AuCl_3} + \underset{149.1}{2\,KCl} + \underset{18.0}{H_2O} = \underset{773.9}{2\,KAuCl_4 \cdot {}^1/_2\, H_2O}$$

An aqueous solution of $AuCl_3$ or $HAuCl_4$, strongly acidified with HCl, is treated with an equimolar quantity of conc. aqueous KCl, and the mixture is evaporated over H_2SO_4 or at a moderately high temperature.

PROPERTIES:

Formula weight 386.94. Light-yellow needles, stable in air. Soluble in water and alcohol, insoluble in ether. Loses water of crystallization at 100°C. Crystal structure: monoclinic.

SYNONYM:

Auric potassium chloride.

REFERENCE:

H. Topsöe. Ber. Wien. Akad. II, 69, 261 (1874).

Gold (III) Oxide

Au_2O_3

$$\underset{496.0}{2\,Au(OH)_3} = \underset{442.0}{Au_2O_3} + \underset{54.0}{3\,H_2O}$$

Gold hydroxide is made according to the procedure outlined in the next preparation and heated to constant weight at 140–150°C.

It is best to start from Au metal if the product must be entirely free of nitrogen oxides. The gold is dissolved in aqua regia and the nitric acid is removed completely by evaporation with hydrochloric acid, repeated five times. The hydroxide is precipitated with a small excess of Na_2CO_3 (very slight blue color on litmus paper), washed several times with water, centrifuged and purified by electrodialysis for 14 days. The product is dried and converted to Au_2O_3 at 140–150°C.

Crystalline Au_2O_3 cannot be obtained by dehydration of $Au(OH)_3$.

Alternate methods: a) By atomization of gold by means of a high-frequency spark in ozonized O_2. The oxidation product contains about 40% Au_2O_3, the rest being elemental Au (see Thiessen and Schütza, as well as Schütza and Schütza, in references below).

b) Precipitation of $Au(OH)_3$ from $AuCl_3$ solution with potassium hydroxide by Fremy's method [W. E. Roseveare and T. F. Buehrer, J. Amer. Chem. Soc. 49, 1221 (1927)].

DETERMINATION OF ACTIVE OXYGEN

The solution is boiled in 0.1N oxalic acid and back-titrated with $KMnO_4$ solution.

SYNONYMS:

Gold trioxide; gold sesquioxide; auric oxide.

PROPERTIES:

Black to brownish black. Soluble in conc. acids, markedly soluble in glacial acetic acid. Decomposes above 160°C into Au and O_2. Heat of formation (25°C): +19.3 kcal./mole.

DropBooks

REFERENCES:

P. A. Thiessen and H. Schiltza. Z. anorg. allg. Chem. 243, 32 (1939); H. Schiltza and I. Schiltza. Z. anorg. allg. Chem. 245, 59 (1940); G. Lunde. Z. anorg. allg. Chem. 163, 345 (1937).

Gold (III) Hydroxide

$Au(OH)_3$

$$\underset{(^1/_2\,H_2O)}{2\,KAuCl_4} + \underset{318.0}{3\,Na_2CO_3} + \underset{54.0}{3\,H_2O}$$
$$= \underset{498.0}{2\,Au(OH)_3} + \underset{350.7}{6\,NaCl} + \underset{149.1}{2\,KCl} + \underset{132.0}{3\,CO_2}$$
(773.9)

A solution of $KAuCl_4$ is heated for several hours on a water bath with an excess of Na_2CO_3. The resultant precipitate is filtered, thoroughly washed, digested with warm, dilute sulfuric acid, and carefully washed in a glass filter crucible until the filtrate is free of H_2SO_4. The product is dried at room temperature over H_2SO_4.

Alternate methods: a) Precipitation of $AuCl_3$ solution with $MgCO_3$ [G. Krüss, Liebigs Ann. 237, 290 (1887)].

b) Hydrolysis of gold sulfate or nitrate [P. Schottländer, Liebigs Ann. 217, 312 (1883)].

c) Fusion of gold with Na_2O_2 and decomposition of the resultant sodium aurate with dilute sulfuric acid [F. Meyer, Compt. Rend. Hebd. Séances Acad. Sci. 145, 805 (1907)].

d) Anodic oxidation of gold in 1N sulfuric acid [F. Jirsa and O. Buryànek, Z. Elektrochem. 29, 126 (1923); W. G. Mixter, J. Amer. Chem. Soc. 33, 688 (191)].

SYNONYM:

Auric hydroxide.

PROPERTIES:

Formula weight 248.02. Brown powder. Insoluble in H_2O, soluble in conc. acids and hot KOH. When dried over P_2O_5 in vacuum, the compound is converted to AuO(OH) (slowly at room temperature, rapidly at 100°C), whereby the color changes, the final one ranging from yellowish red to ocher-brown. Converts to Au_2O_3 at 140–150°C.

REFERENCE:

R. Lydén. Z. anorg. allg. Chem. 240, 157 (1939).

Potassium Aurate

$KAuO_2 \cdot 3\,H_2O$

$$\underset{496.0}{2\,Au(OH)_3} + \underset{112.2}{2\,KOH} + \underset{36.0}{2\,H_2O} = \underset{644.3}{2\,KAuO_2 \cdot 3\,H_2O}$$

Auric hydroxide is reacted with warm conc. KOH in the absence of atmospheric CO_2. After filtration the solution is allowed to evaporate in the dark. The precipitated crystals are dried in vacuum over H_2SO_4.

PROPERTIES:

Formula weight 322.15. Light-yellow needles, soluble in water, giving a highly alkaline reaction. Decomposes on gentle heating, giving off water and oxygen. The residue consists of Au, KOH and KO_2.

DropBooks

REFERENCES:

F. Meyer, Compt. Rend. Séances Acad. Sci. 145, 805 (1907); E. Frémy. Ann. Chim. Phys. 31, 483 (1853).

Gold (I) Sulfide

Au_2S

$$\underset{576.3}{2\,K[Au(CN)_2]} + \underset{22.41.}{H_2S} + \underset{72.9}{2\,HCl} = \underset{428.1}{Au_2S} + \underset{149.1}{2\,KCl} + \underset{108.1}{4\,HCN}$$

A conc. solution of $K[Au(CN)_2]$, obtained by treatment of a solution of $AuCl_3$ with excess KCN, is saturated with H_2S. Hydrochloric acid is added to the clear solution and the mixture is heated, resulting in the appearance of a brown color. A heavy, rapidly settling precipitate is formed on boiling. This is filtered, washed with water, and then successively with alcohol, ether, CS_2 and finally again with ether. The product is dried to constant weight over P_2O_5.

The product usually contains sulfur and some moisture, which are difficult to remove. It may be freed of S by dissolving in KCN, filtering and reprecipitating with boiling hydrochloric acids.

PROPERTIES:

Brown-black powder when dry, steel-gray when moist. The freshly precipitated compound is readily soluble in water, forming a colloid, particularly in the presence of H_2S. Easily recoagulated by hydrochloric acid and salts. Insoluble after drying over P_2O_5. Resistant to conc. hydrochloric acid and H_2SO_4, as well as to KOH. Oxidized by aqua regia and strong oxidants. Soluble in solutions of KCN and alkali polysulfides. Decomposes at 240°C into Au and S.

REFERENCE:

L. Hoffmann and G. Krüss. Ber. dtsch. chem. Ges. 20, 2361 (1887).

Gold (II) Sulfide

AuS

	$8\,AuCl_3$	+	$9\,H_2S$	+	$4\,H_2O$	=	$8\,AuS$	+	$24\,HCl$	+	H_2SO_4
Wt.	242.7		20.21.		7.2		183.3		87.5		9.8

A neutral 1-3% solution of $AuCl_3$ is precipitated in the cold (the temperature must not exceed 40°C) with H_2S or an alkali sulfide. The precipitate is filtered, thoroughly washed with water, and treated with alcohol, anhydrous ether, CS_2 and again with ether. The product is dried at 130°C over P_2O_5.

Alternate method: A solution of $AuCl_3$ is added in drops to an aqueous solution of sodium dithiosulfatoaurate (I) (for preparation, see under Au_2C_2) (Antony and Lucchesi, see references below).

PROPERTIES:

Formula weight 229.07. Deep black. Insoluble in water and acids; soluble in aqua regia and solutions of potassium cyanide and alkali polysulfides. Resistant to KOH in the cold, decomposes after prolonged boiling, liberating gold. Thermal decomposition begins at 140°C.

REFERENCES:

U. Antony and A. Lucchesi. Gazz. Chim. Ital. 19, 552 (1889); 20, 61 (1890); L. Hoffmann and G. Krüss. Ber. dtsch. chem. Ges. 20, 2704 (1887).

Gold (III) Sulfide

Au_2S_3

$$\underset{(4\,H_2O)}{2\,HAuCl_4} + 3\,H_2S = Au_2S_3 + 8\,HCl$$

823.8 67.21. 490.2 291.7

A fast stream of H_2S is introduced into 1N hydrochloric acid at −2 to −4°C; simultaneously, a cooled solution of $HAuCl_4 \cdot 4\,H_2O$ is allowed to flow in. The black precipitate is digested with water, washed free of acid, treated with alcohol and ether, extracted with CS_2 in a Soxhlet extractor, washed with ether, and dried in vacuum over P_2O_5.

Alternate methods: a) A solution of $AuCl_3$ in absolute ether is saturated with H_2S. The product is washed with CS_2 and alcohol [K. A. Hofmann and F. Höchtlen, Ber. dtsch. chem. Ges. 37, 245 (1904)].

b) Completely dry $LiAuCl_4 \cdot 2\,H_2O$ is treated with H_2S at −10°C. The product is extracted with alcohol, CS_2, and again with alcohol and ether, and dried at 70°C in pure N_2 [U. Antony and A. Lucchesi, Gazz. Chim. Ital. 19, 552 (1889)].

PROPERTIES:

Deep black. Insoluble in water. Resistant to hydrochloric and sulfuric acids and dilute nitric acid. Vigorous reaction with conc. nitric acid. Soluble in conc. Na_2S solution, alkali polysulfides and KCN. d_4^{20} 8.754.

DropBooks

REFERENCE:

A. Gutbier and E. Dürrwächter. Z. anorg. allg. Chem. 121, 266 (1922).

Gold (I) Acetylide

Au_2C_2

Prepared by precipitating a solution of sodium dithiosulfatoaurate (I), $Na_3[Au(S_2O_3)_2] \cdot 2\,H_2O$, with acetylene.

A) SODIUM DITHIOSULFATOAURATE (I)

A solution of 3 parts of $Na_2S_2O_3 \cdot 5\,H_2O$ in 50 parts of water is reacted (stirring) with a solution of 1 part of $AuCl_3$ in 50 parts

of water. The gold solution is added in portions, each portion being added only after the red color resulting from the previous addition has disappeared. The compound is precipitated from this solution with 96% alcohol and purified by repeated solution in water and reprecipitation with alcohol.

B) GOLD (I) ACETYLIDE

A solution of $Na_3[Au(S_2O_3)_2]$ is reacted with an excess of strong aqueous ammonia and then slowly saturated with C_2H_2. The solution becomes yellow, and a yellow precipitate deposits after some time. It is washed by decantation with water and alcohol, filtered and dried over H_2SO_4.

PROPERTIES:

Formula weight 418.02. Yellow powder. Insoluble in water; decomposes in boiling water without evolution of C_2H_2; decomposes slightly in hydrochloric acid with evolution of C_2H_2. Extremely explosive when dry. Detonates at 83°C if rapidly heated.

REFERENCE:

A. Mathews and L. L. Watters. J. Amer. Chem. Soc. 22, 108 (1900).

Gold (I) Cyanide

AuCN

$$\underset{288.1}{K[Au(CN)_2]} + \underset{36.5}{HCl} = \underset{223.0}{AuCN} + \underset{27.0}{HCN} + \underset{74.6}{KCl}$$

An aqueous solution of $K[Au(CN)_2]$ is mixed in the cold with hydrochloric acid and warmed to 50°C. Most of the AuCN precipitates. The mixture is evaporated to dryness on a steam bath, resulting in removal of HCN. The residue is taken up in water, filtered, thoroughly washed (in the absence of sunlight) to remove KCl, and dried over H_2SO_4 or P_2O_5.

Alternate methods: a) Precipitation of a solution of $AuCl_3$ with KCN [P. O. Figuier, J. Pharm. Chim. 22, 329 (1836)].

b) Decomposition of $Na[Au(CN)_2]$ with HCl [A. Wogrinz, Metalloberfläche 8, 11, 162 (1954)].

PROPERTIES:

Lemon-yellow crystalline powder. Stable in air. Sparingly soluble in water and dilute acids. Soluble in solutions of alkali

cyanides, KOH, ammonia, $Na_2S_2O_3$ and $(NH_4)_2S$. Decomposes with separation of Au on dry heating. Unstable in light when moist. d_4^{20} 7.12. Crystal structure: hexagonal.

REFERENCE:

K. Himly. Liebigs Ann. 42, 157 (1842).

Potassium Dicyanoaurate (I)

$K[Au(CN)_2]$

Formed when "fulminating gold" is dissolved.

Pure gold (10 g.) is dissolved in 50 ml. of aqua regia (34 ml. of conc. hydrochloric acid and 16 ml. of nitric acid, d 1.33) on a steam bath. When solution is complete (after about two hours), "fulminating gold" is precipitated by addition of an excess of ammonia. It is washed until Cl-free, dissolved while still moist in a slight excess of KCN solution, concentrated on a steam bath, and allowed to crystallize overnight. Additional salt may be recovered from the mother liquor. The product is recrystallized from an equal amount of boiling water, and dried over P_2O_5 or conc. H_2SO_4. Yield 90%.

Alternate methods: a) Electrolytic solution of Au in warm aqueous KCN [J. Glassford and J. Napier, Phil. Mag. 25, 61 (1844)].

b) To prepare solutions of $K[Au(CN)_2]$ or $Na[Au(CN)_2]$ for use in gold-plating baths and still avoid using gold sponge or evolution of HCN, $HAuCl_4$, in an amount corresponding to 3 parts by weight of Au, is dissolved in 50 parts by weight of water. The flask contents are swirled around while Na_2CO_3 or K_2CO_3 is added until a test with Congo paper no longer yields a blue color. The gold solution is then poured into a porcelain dish and allowed to react (stirring) with 5.2 parts by weight of NaCN or 6.8 parts of KCN; the solution becomes warm and colorless. Six parts of annealed 0.02-mm.-thick gold foil, cut into small chips, are added, and the mixture is heated for several hours on a water bath with stirring and replenishing of the evaporating water. Residual unreacted gold is removed and the solution is evaporated to dryness [A. Wogrinz, Prakt. Chem. (Vienna) 3, 216 (1952)].

SYNONYM:

Gold potassium cyanide.

PROPERTIES:

Formula weight 288.14. Colorless crystals. Readily soluble in H_2O, sparingly soluble in alcohol, insoluble in ether and acetone.

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Precipitated from saturated aqueous solution by sulfuric acid, hydrochloric acid, nitric acid and alcohol. Decomposes on boiling with acids. Stable in air and light. $d_4^{25°}$ 3.45.

REFERENCE:

F. Chemnetius. Chemiker-Ztg. 51, 823 (1927).

SECTION 20

Zinc, Cadmium, Mercury

F. WAGENKNECHT AND R. JUZA*

Zinc

Zn

VERY PURE ZINC

Certain grades of commercial zinc are quite pure. The highest purity may be achieved by distillation (Procedure I) or, starting from $ZnSO_4$, by purification of the salt and electrolytic isolation of the metal (Procedures I and II). Extreme purity of zinc salts is particularly important in the preparation of scintillators.

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I. PURIFICATION OF ZINC SULFATE IN SOLUTION

Alumina, standardized by the method of Brockmann, is introduced in portions into a glass tube (30 cm. long, 4 cm. diameter) provided with a fritted glass disk at one end. After each addition the adsorbent is compacted with a glass pestle or by applying a vacuum. The material is allowed to fill 2/3 to 4/5 of the tube length. The material is prevented from fluidizing by placing a piece of filter paper on top. The flask containing the solution is above the column; the liquid flows into the column through an inlet tube bent at an acute angle. The bottom end of the column is placed in a suction flask. Continuous operation of the system is achieved by applying a slight vacuum. The adsorbent removes As, Sb, Bi, Cr, Fe, Hg, U, Pb, Cu and Ag.

To remove Ni or Co, the $ZnSO_4$ solution is made alkaline with ammonia and filtered through alumina that has been pretreated with an alcoholic solution of, respectively, diacetyldioxime or 1-nitroso-β-naphthol.

Manganese may be removed by adding to the $ZnSO_4$ solution 0.5 g. of $(NH_4)_2PbCl_6$ hydrolyzed in one liter of redistilled (I) H_2O, heating the mixture for a short time to the boiling point.

*The second edition was revised by Dr. H. U. Schuster.

and filtering off the deposit of PbO_2 flakes after 24 hours. Traces of the Pb are removed by passing the solution through an Al_2O_3 column and concentrating the product. Solutions purified with Al_2O_3 as above satisfy the most stringent requirements.

II. ELECTROLYTIC SEPARATION

The electrolyte should contain 40-60 g./liter of Zn (calculated as the sulfate). A piece of silk taffeta serves as the membrane. Pure ZnO is suspended by stirring in the anode chamber. The cathode is Al or Pt, the anode is Pt. The current density is 0.01-0.03 amp./cm.^{2} The Zn deposit may be peeled off cleanly from the aluminum sheet by cutting off its edges. Inclusions are removed by fusing with a small quantity of NH_4Cl in a porcelain crucible. The ingot is pickled clean with HCl and thoroughly washed with distilled water.

III. DISTILLATION OF METALLIC ZINC

The last step in the purification of the Zn metal is a double vacuum distillation. The operation is carried out in a Vycor tube shaped as in Fig. 280. After the distillation (650°C), a slight gray deposit, which is separate from the main body of the distillate, may be observed at *b*. It contains Cd. Traces of a black, very fluffy impurity are left at *a*. No impurity deposit is formed at *b* during the subsequent second distillation. To prevent contamination of the final product with some heavy, low-volatility components still present, the second distillation is stopped before the material at *a* is depleted. The resultant Zn product is spectroscopically pure. If a quartz tube is used and larger amounts of Zn (e.g., 30 g.) are distilled, the distillate adheres very strongly to the tube wall.

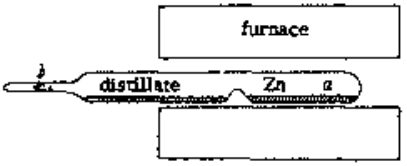

Fig. 280. Distillation of zinc.

PROPERTIES:

Atomic weight 65.38. Bluish white. Solubility in Hg (18°C) 2.2 g. Zn/100 g. Hg. M.p. 419.4°C, b.p. 905.7°C; d 7.133. Hardness 2.5. Crystal structure: type A3 (Mg type). Electrochemical equivalent 1.220 g. $(amp. \cdot hr.)^{-1}$.

REFERENCES:

1. E. Tiede and W. Schikore, Ber. dtsch. chem. Ges. 75, 586 (1942); W. Schikore and E. G. Müller, Z. anorg. Chem. 255,

327 (1948); W. Schikore and T. Pankow. Ibid. 258, 15 (1949).
II. F. Mylius and O. Fromm. Z. anorg. allg. Chem. 9, 144 (1895).
III. R. Petermann. Thesis, Bern, 1946; O. Hönigschmid and M. von Mack. Z. anorg. allg. Chem. 246, 363 (1941).

Zinc Hydride

ZnH_2

I. $$\underset{319.2}{ZnI_2} + 2\,\underset{75.8}{LiAlH_4} = \underset{67.4}{ZnH_2} + 2\,\underset{59.9}{AlH_3} + 2\,\underset{287.7}{LiI}$$

Ether solutions of ZnI_2 and $LiAlH_4$ (mole ratio 1:2) are mixed at −40°C or below; a white precipitate forms. The product must be separated immediately by centrifugation to prevent contamination by polymeric $(AlH_3)_x$, which begins to form after some time. The LiI remains in the supernatant solution.

II. $$\underset{95.4}{Zn(CH_3)_2} + 2\,\underset{75.9}{LiAlH_4} = \underset{67.4}{ZnH_2} + 2\,\underset{103.9}{LiAlH_3CH_3}$$

Dimethylzinc (0.57 g., ~6 mmoles) is distilled in a completely dry atmosphere into an ice-cold solution of 0.59 g. (~15.6 mmoles) of $LiAlH_4$ in 10 g. of absolute ether (predried over $LiAlH_4$). The white precipitate obtained on heating the mixture to room temperature is filtered, washed several times with absolute ether, and freed of adhering ether by heating to 50°C in vacuum.

The dimethylzinc needed for this preparation is obtained by heating $Hg(CH_3)_2$ (p. 1119) with a large excess of zinc shot in a closed tube. At 120°C the yield is quantitative after 64 hours. The dimethylzinc may be distilled at atmospheric pressure in a stream of N_2. B.p. 46°C.

PROPERTIES:

Solid, white, nonvolatile when pure. Readily oxidized; reacts with H_2O or humid air, evolving H_2. This reaction is very vigorous in the case of old preparations, which often ignite spontaneously. Stable for some time at room temperature in dry air; in high vacuum at 90°C, gradually decomposes to the elements.

REFERENCES:

I. W. Wiberg, W. Henle and R. Bauer. Z. Naturforschg. 6b, 393 (1951).
II. G. D. Barbaras, A. E. Finholt, H. J. Schlesinger et al., J. Amer. Chem. Soc. 73, 4585 (1951).

Zinc Chloride

$ZnCl_2$

$$\underset{65.4}{Zn} + 2\,\underset{72.9}{HCl} = \underset{136.3}{ZnCl_2} + \underset{2.0}{H_2}$$

I. Very pure, anhydrous $ZnCl_2$ is prepared by treating Zn with dry HCl at 700°C in a quartz boat placed in a tube of high-melting glass. At this temperature, the formation and sublimation of $ZnCl_2$ proceed at sufficiently high rates. The sublimed chloride is collected in a section of the tube which is kept cool for this purpose. Temperatures above 700°C should be avoided, since entrainment of zinc vapor with the chloride may result, a phenomenon recognizable by the appearance of a color in the otherwise colorless sublimate. For additional purification, the chloride may be resublimed in a stream of HCl.

II. The same reaction can be carried out in anhydrous ether. Ether and excess HCl are removed on a steam bath (vacuum).

III.
$$\underset{65.4}{Zn} + 2\,\underset{198.0}{CuCl} = \underset{136.3}{ZnCl_2} + 2\,\underset{127.1}{Cu}$$

A 6.7% solution of CuCl in pure, dry acetonitrile (distilled several times over P_2O_5) is electrolyzed at room temperature with a Pt cathode and a Zn anode (voltage across the terminals is 12 v.). The electrolysis proceeds under a blanket of absolutely dry N_2. The reaction is complete when a gray coating of Zn is observed on the Cu deposited at the cathode. The solvent is evaporated in vacuo, and the acetonitrile solvate of $ZnCl_2$ is converted into the unsolvated salt by careful heating. Yield 96-98%.

If the appropriate copper salts are used, the process may also be employed for the preparation of $ZnBr_2$ and ZnI_2, and by substituting a cadmium anode for the zinc electrode, $CdBr_2$ and CdI_2 may be prepared.

Zinc chloride exists in three different crystal modifications. Details on the preparation and the structure of the pure individual modifications are given by H. R. Oswald and H. Jaggi [Helv. Chim. Acta 43, 72 (1960)].

PROPERTIES:

Colorless, highly hygroscopic, small crystals. M.p. 313°C, b.p. 732°C; d (pycn.) 2.93. Solubility per 100 ml. of H_2O: (0°C) 208 g., (20°C) 367 g. (d 2.08), (100°C) 614 g. Crystallizes in the

anhydrous form only above 28°C. Soluble in methanol, ethanol, ether, acetone and other organic solvents.

REFERENCES:

I. O. Hönigschmid and M. von Mack. Z. anorg. allg. Chem. 246, 366 (1941); for apparatus, see O. Hönigschmid and F. Wittner. Ibid. 226, 295 (1936).
II. R. T. Hamilton and J. A. V. Butler. J. Chem. Soc. (London) 1932, 2283.
III. H. Schmidt. Z. anorg. allg. Chem. 271, 305 (1953).

Zinc Hydroxychloride

$Zn(OH)Cl$

$$\underset{81.4}{ZnO} + \underset{136.3}{ZnCl_2} + \underset{18.0}{H_2O} = 2\,\underset{235.7}{Zn(OH)Cl}$$

Zinc hydroxychloride is one of the basic zinc halides which can be prepared as well-defined crystalline compounds by several methods, for example, by dissolving ZnO in zinc halide solutions of definite concentration.

The compound is prepared by adding 6–7 g. of ZnO to 100 ml. of a 70% solution of $ZnCl_2$ and heating to about 150°C until solution is complete. (If seeding crystals are present, the solution becomes turbid and crystallization begins at 133°C.) A coarsely crystalline product is obtained by cooling the solution to 50°C (where the first crystals separate), then heating to 135°C and allowing the mixture to cool slowly to room temperature over a period of 24 hours. Most of the crystals deposit between 130 and 100°C. The mass is carefully crushed and washed with acetone until the filtrate exhibits only a weak opalescence on addition of $AgNO_3$. The product is dried in vacuum over $CaCl_2$.

SYNONYM:

Zinc chloride hydroxide.

PROPERTIES:

Formula weight 117.85. Colorless hexagonal leaflets. The chloride content is removed by water.

REFERENCES:

Driot. Comptes Rendus Hebd. Séances Acad. Sci. 150, 1426 (1910); W. Feitknecht. Helv. Chim. Acta 13, 22 (1930).

DropBooks

Ammonium Tetrachlorozincate

$(NH_4)_2ZnCl_4$

$$\underset{136.3}{ZnCl_2} + \underset{107.0}{2\,NH_4Cl} = \underset{243.3}{(NH_4)_2ZnCl_4}$$

A solution of 70 g. of $ZnCl_2$ and 30 g. of NH_4Cl is prepared by heating with 29 (!) ml. of hot H_2O. It is advisable to measure the water with a balance. The homogeneous diammonium salt crystallizes on cooling. Yield 45 g.

The three-component system $ZnCl_2$-NH_4Cl-H_2O has been investigated by Meerburg. It was found that $(NH_4)_2ZnCl_4$ can be precipitated only from solutions which have higher concentrations of $ZnCl_2$ than the desired salt. A solution containing $ZnCl_2$ and NH_4Cl in a 1:2 ratio usually yields the salt $ZnCl_2 \cdot 3\,NH_4Cl$.

PROPERTIES:

Shiny, orthorhombic leaflets, crystallizable only from $ZnCl_2$ solutions. M.p. ~ 150°C; d 1.88. Crystal class D_{2h}.

REFERENCE:

P. A. Meerburg, Z. anorg. allg. Chem. 37, 199 (1903).

Zinc Bromide

$ZnBr_2$

$$\underset{65.4}{Zn} + \underset{80.9}{HBr} + \underset{79.9}{{}^1/_2Br_2} = \underset{225.2}{ZnBr_2} + {}^1/_2H_2$$

The purest material is obtained by electrolytically dissolving purified Zn in a mixture of aqueous HBr and Br_2 in a quartz dish. The solution is digested with an excess of Zn, filtered and crystallized by evaporation. The crystals are recrystallized from dilute hydrobromic acid and separated from the mother liquor by centrifugation. The product is then sublimed in a stream of HBr-N_2.

Alternate method: See under zinc chloride, p. 1070.

PROPERTIES:

Colorless, highly hygroscopic crystals. Sublimes, producing lustrous needles. M.p. 394°C, b.p. 650°C; d 4.201. Solubility (0°C)

388 g. (2 H_2O); (100°C) 675 g. (anhydrous $ZnBr_2$)/100 ml. H_2O. Anhydrous when crystallized above 37°C. Soluble in alcohol and ether. Crystal structure: tetragonal; space group $I4_1/acd$.

REFERENCES:

G. P. Baxter and M. R. Grose. J. Amer. Chem. Soc. 38, 868 (1916); G. P. Baxter and J. R. Hodges. Ibid. 43, 1242 (1921).

Zinc Iodide

ZnI_2

$$Zn + I_2 = ZnI_2$$
$$65.4 \quad 253.8 \quad 319.2$$

I. One part of zinc dust is digested with three parts of iodine and 10 parts of H_2O until disappearance of the I_2. The mixture is filtered and concentrated over H_2SO_4 and NaOH in a vacuum desiccator (N_2 atmosphere). The ZnI_2 which crystallizes out is vacuum-distilled at about 400°C.

Well-dried ZnI_2, prepared by the wet method, is sublimed in an oil-pump vacuum. The evolving iodine is expelled from the apparatus. The compound is obtained as a pure white sublimate.

II. One part of zinc dust is refluxed with two to four parts (depending on the quality of the Zn dust) of iodine and 10 parts of absolutely anhydrous ether until the initial coloration of the liquid disappears completely. The residual Zn-ZnO slurry is removed from the ether solution by filtration through a fritted glass filter. Most of the ether is distilled off, leaving a product containing about 0.5 mole of ether per mole; the ether is driven off in vacuum (fanning of the flask with a flame will help).

Alternate method: See under zinc chloride, p. 1070.

PROPERTIES:

Colorless, highly hygroscopic crystals. M.p. 446°C, b.p. 624°C; d 4.736. Solubility (18°C) 432 g.; (100°C) 510 g. (anhydrous salt)/100 ml. H_2O. Below 0°C, $ZnI_2 \cdot 2H_2O$ crystallizes out of solution. Soluble in ethanol, ether, acetone and dioxane. Sublimes in vacuum (crystal needles). Decomposes on heating in air. Crystal structure: tetragonal; space group $I4_1/acd$.

REFERENCES:

I. T. J. Webb, J. Phys. Chem. 27, 450 (1923); W. Biltz and C. Messerknecht, Z. anorg. allg. Chem. 129, 161 (1923).
II. Unpublished experiments of P. Laurer and R. Platz, Heidelberg.

Zinc Hydroxide

(crystalline)

ϵ-$Zn(OH)_2$

I. $\underset{81.4}{ZnO} - \underset{40.0}{NaOH} + \underset{18.0}{H_2O} = \underset{139.4}{NaZn(OH)_3} = \underset{99.4}{Zn(OH)_2} + \underset{40.0}{NaOH}$

Analytical grade ZnO (160 g.) is refluxed in a round-bottom flask containing a solution of 600 g. of NaOH in 300 ml. of H_2O. After the ZnO is dissolved, the solution is diluted with 300 ml. of H_2O and cooled to 60°C. At this point, the volume of the solution is about 900 ml. It is filtered and diluted 10 times with water. Crystalline $Zn(OH)_2$ separates out after 2–3 weeks. This is filtered, washed first with cold water, then several times with warm water, and dried over conc. H_2SO_4.

Small needles are formed during the initial stages of crystallization; however, standing converts them into the other crystal form.

II. Amorphous $Zn(OH)_2$ is prepared by adding the stoichiometric quantity of ammonia to a solution containing a known quantity of $ZnSO_4$. The precipitate is filtered and washed thoroughly to remove as much of the adsorbed sulfate as possible [if the $Zn(OH)_2$ is worked up without preliminary washing, the product consists of basic sulfates]. The moist, washed precipitate is dissolved in the required amount of conc. ammonia. Then NH_3 is slowly separated from the solution by placing the beaker with the ammonia solution together with a beaker with H_2SO_4 under a bell jar. A large quantity of crystals is obtained within a week. It is important that the initial removal of NH_3 be slow; then the resultant crystals are 0.5 cm. long, on the average.

PROPERTIES:

Colorless crystals. In equilibrium with water, stable up to **29°C; decomposes** at higher temperature. d 3.053. Crystal structure: **type C31** [ϵ-$Zn(OH)_2$ type].

In addition to the stable ϵ-$Zn(OH)_2$, there are five additional crystalline forms of the compound, which are unstable and convert spontaneously to ϵ-$Zn(OH)_2$.

REFERENCES:

I. R. Scholder and G. Hendrich. Z. anorg. allg. Chem. 241, 76 (1939).

II. H. G. Dietrich and J. Johnston. J. Amer. Chem. Soc. 49, 1419 (1927).

Zinc Sulfide

ZnS

$$\underset{(7\,H_2O)}{ZnSO_4} + H_2S = ZnS + H_2SO_4$$

287.6 22.4 *l.* 97.4 98.1

I. Zinc sulfide is preferably precipitated from a slightly acidic buffered aqueous solution: an aqueous solution of $ZnSO_4$ is treated with ammonium acetate; it is then saturated with H_2S with heating and frequent stirring (optimum pH for precipitation: 2-3). The precipitate is allowed to settle and the supernatant is decanted. The precipitate is shaken with 2% acetic acid saturated with H_2S; the solid is allowed to settle and the washing is repeated. To obtain an oxide-free product, the filtration and drying should be carried out in the absence of air.

II. Well-crystallized zincblende is obtained from pure, dry precipitated zinc sulfide by heating the sulfide in a stream of nitrogen for eight hours at 600-650°C. The reactor is a ceramic tube.

Pure wurtzite may be prepared from the same ZnS precipitate by heating in a stream of N_2 for one hour at 1150°C.

PROPERTIES:

White powder. M.p. ~ 1650°C (appreciable volatilization); distills without decomposition at high vacuum ($5 \cdot 10^{-4}$ mm.). d 4.14. Solubility (18°C) 0.688 mg. (freshly precipitated)/100 ml. H_2O. Soluble in dilute mineral acids. Hardness 3.5-4 (both modifications). The low-temperature modification (sphalerite) crystallizes in the cubic B3 system (zincblende), the high-temperature modification (wurtzite) in the hexagonal B4 system. Transition point: about 900°C. Grinding at room temperature converts the metastable wurtzite to zincblende.

REFERENCE:

H. Plata and P. W. Schenk. Angew. Chem. 49, 822 (1936).

Zinc Formaldehydesulfoxylate

$Zn(SO_2 \cdot CH_2OH)_2$

$$\underset{387.0}{2\,ZnS_2O_4} + \underset{120.1}{4\,CH_2O} + \underset{36.0}{2\,H_2O} = \underset{255.6}{Zn(SO_2 \cdot CH_2OH)_2} + \underset{287.6}{Zn(SO_3 \cdot CH_2OH)_2}$$

A 33% solution of ZnS_2O_4 (1300 g.) is added to 600 g. of a 30% formaldehyde solution; the addition is accompanied by a temperature rise to 50°C. The liquid is stirred and the temperature maintained at 60–65°C for some time. The mixture is filtered and set aside for 2–3 days. The clear solution is again filtered and concentrated in vacuum while SO_2 is aspirated in through a boiling capillary. The zinc formaldehydesulfoxylate is the first to precipitate. The crystals are separated from the mother liquor by centrifugation and dried by heating in vacuum.

The trihydrate is obtained at 60°C from a solution of 100 g. of the anhydrous salt in 100 ml. of H_2O, the tetrahydrate by allowing a solution saturated at 20°C to stand for some time.

The ZnS_2O_4 solution required in the preparation cannot be prepared according to the directions given on p. 394, since the latter procedure yields aqueous solutions containing only about 10% ZnS_2O_4. In this case it is better to react a mixture of the purest possible Zn dust (200 g.) and H_2O (400 ml.) with SO_2, which should be prewashed with an alkaline solution of $Na_2S_2O_4$. The reaction proceeds according to:

$$\underset{65.4}{Zn} + \underset{128.1}{2\,SO_2} = \underset{193.5}{ZnS_2O_4}$$

and is carried out in a wide-neck Erlenmeyer flask at 35–40°C (stirring). Initially, the mixture must be cooled; later it should be warmed. After several hours the reaction slurry is allowed to settle and the product is filtered through a Buchner funnel. The concentration of the viscous, unstable solution is determined by titration with a 0.01 M solution of indigo carmine [1 mole of indigo is equivalent to 1 mole of $S_2O_4^{2-}$; for additional analytical methods see G. Panizzon, Melliand Textilber. 12, 119 (1931)].

A method for the preparation of secondary zinc formaldehydesulfoxylate is described in M. Bazlen, Ber. Dtsch. chem. Ges. 60, 1470 (1927); cf. also K. Jellinek, Das Hydrosulfit [Hydroxysulfite]. Part II, Stuttgart, 1912.

SYNONYMS:

Primary zinc oxymethanesulfinate; monozinc formaldehydesulfoxylate.

A technical-grade product containing over 90% of the anhydrous compound is available under the names Dekrolin soluble conc. (BASF), water-soluble Hydrosulfit BZ (Ciba), Sulfoxite S conc. (Du Pont), etc.

PROPERTIES:

Colorless crystal needles. The anhydrous salt is stable in air. The trihydrate (flakes with a nacreous luster) and the tetrahydrate (rhombohedral leaflets) are more labile. Soluble in H_2O. The solution acts as a bleaching agent and is quite resistant to acids. The reducing activity increases markedly with temperature; the rH values of a formic acid solution at pH 3 are: (25°C) 15; (50°C) 2; (90°C) a maximum of 0.5. Decomposes on prolonged boiling. The warm solution turns alkaline indanthrene yellow G paper blue and decolorizes an alcoholic solution of neutral red.

REFERENCES:

K. Winnacker and E. Weingaertner, Chem. Technologie, Vol. 2, p. 80, Munich, 1950; BIOS Final Report No. 422, London, 1945; H. von Fehling, Neues Handwörterb. d. Chemie [New Handbook of Chemistry], Vol. X, p. 291, Braunschweig, 1930; A. Schaeffer, Melliand Textilber. 30, 111 (1949).

DigiBooks

Ammonium Zinc Sulfate

$$(NH_4)_2Zn(SO_4)_2 \cdot 6\,H_2O$$

$$\underset{132.1}{(NH_4)_2SO_4} + \underset{287.6}{ZnSO_4 \cdot 7\,H_2O} = \underset{401.7}{(NH_4)_2Zn(SO_4)_2 \cdot 6\,H_2O} + \underset{18.0}{H_2O}$$

A solution of 45.2 g. of $ZnSO_4 \cdot 7H_2O$ and 20.8 g. of $(NH_4)_2SO_4$ is prepared in 75 ml. of boiling H_2O. The solution is filtered through a jacketed funnel heated with hot water. The crystals precipitating from the filtrate are separated from the mother liquor and dried in vacuum over anhydrous ammonium zinc sulfate or H_2SO_4. Yield 50 g.

PROPERTIES:

Water-clear, efflorescent, monoclinic crystals. Solubility of the anhydrous salt (0°C) 7.3 g.; (20°C) 12.6 g.; (85°C) 46.2 g. per 100 ml. H_2O. d 1.93. Space group C_{2h}^5.

Zinc Selenide

ZnSe

$$\underset{(7\,H_2O)}{ZnSO_4} + H_2Se = ZnSe + H_2SO_4$$
$$\underset{287.6}{} \quad \underset{22.4\,l.}{} \quad \underset{144.3}{} \quad \underset{98.1}{}$$

I. A dilute solution of $ZnSO_4$, buffered with ammonium acetate, is added dropwise to a saturated aqueous solution of H_2Se, while a stream of H_2Se (from Al_2Se_3 and dilute HCl), diluted with oxygen-free N_2 or H_2, is passed through the liquid. The precipitation vessel is heated on a steam bath. The excess H_2Se bubbling out of the solution is absorbed in a wash bottle filled with conc. nitric acid. If the Zn salt solution is introduced too rapidly or in too high a concentration, a white precipitate is formed; it requires a very long time to convert to the yellow ZnSe. Since the yellow ZnSe precipitate is difficult to filter, it is centrifuged and then washed (by centrifugation) first with boiled, weakly ammoniacal H_2O and then with methanol. It is dried in a vacuum desiccator over $CaCl_2$, then at 120°C in a drying pistol over P_2O_5.

When moist, zinc selenide is very sensitive to air. Therefore, to remove oxidation products the dry product is placed in a tube and heated for 2-4 hours at 600°C in a stream of H_2 or H_2Se. A boat containing a small amount of Se is placed ahead of the product. The heating is continued until all the Se in the boat evaporates. The cubic modification is thus obtained.

The hexagonal modification is obtained by treating $ZnCl_2$ vapor with H_2Se.

II. ZnSe may be prepared by a dry method from a mixture of 4 g. of ZnO, 2.5 g. of ZnS, and 6 g. of Se according to:

$$\underset{162.7}{2\,ZnO} + \underset{97.4}{ZnS} + \underset{236.9}{3\,Se} = \underset{433.0}{3\,ZnSe} + \underset{64.1}{SO_2}$$

The mixture is heated for 15 minutes at 800°C in a covered quartz crucible.

It is also possible to start from 5 g. of ZnS and 6.5 g. of H_2SeO_3, and then proceed as above. The reaction is formulated as:

$$\underset{97.4}{ZnS} + \underset{111.0}{SeO_2} = \underset{144.3}{ZnSe} + \underset{64.1}{SO_2}$$

PROPERTIES:

Lemon-yellow powder. Soluble in fuming hydrochloric acid with evolution of H_2Se. d (pycn.) 5.30. Crystal structure: type B3 (zincblende type) or B4 (wurtzite type).

REFERENCES:

I. R. Juza, A. Rabenau and G. Pascher. Z. anorg. allg. Chem. 285, 61 (1956); Fonzes-Diacon. Comptes Rendus Hebd. Séances Acad. Sci. 130, 832 (1900).
II. A. Schleede and J. Glassner. German Patent 699,320 (1938), issued to Telefunken Co.

Zinc Amide

$Zn(NH_2)_2$

$$\underset{123.5}{Zn(C_2H_5)_2} + \underset{34.1}{2\,NH_3} = \underset{97.4}{Zn(NH_2)_2} + \underset{60.1}{2\,C_2H_6}$$

The preparation is carried out in the apparatus of Fig. 281. Diethylzinc is introduced into the storage vessel through the side tube, a blanket of CO_2 being provided; the side tube is then sealed. For each run, about 3 g. of $Zn(C_2H_5)_2$ is vacuum-distilled from *a* to *b*. The apparatus is then filled through stopcock *c* with very pure N_2. The tube connecting the two vessels is broken at *d*, and 50 ml. of absolute ether, carefully dried with Na wire, is added through *e*. During these manipulations, the system is flushed with a fast stream of N_2, which is introduced at *c* and leaves the apparatus through a $CaCl_2$ tube attached at *d*. The $Zn(NH_2)_2$ is precipitated from the ether solution by a stream of carefully purified NH_3. Simultaneously, the ether in *b* is evaporated, an operation which requires about two hours. The product is comminuted by shaking (glass slug *f* is already present in *b*). Ammonia is then passed over the product for five hours at 150°C and for 12 hours at room temperature.

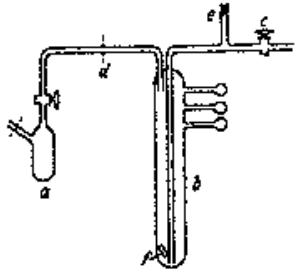

Fig. 281. Preparation of zinc amide. *a* storage vessel for diethylzinc; *f* glass slug.

PROPERTIES:

Colorless, amorphous; decomposes slowly in air. d 2.13.

REFERENCE:

R. Juza, K. Fasold and W. Kuhn. Z. anorg. allg. Chem. 234, 86 (1937).

Zinc Nitride

Zn_3N_2

$$\underset{196.1}{3\,Zn} + \underset{34.1}{2\,NH_3} = \underset{224.2}{Zn_3N_2} + \underset{6.1}{3\,H_2}$$

A porcelain boat containing ~7 g. of zinc dust is placed in a Vycor tube. The material is heated in a rapid stream of NH_3 for 17 hours at 500°C, for eight hours at 550°C, and finally for 16 hours at 600°C. In the process, about 3 g. of Zn is lost by distillation. The remainder is converted to Zn_3N_2. This procedure assumes that the zinc does not fuse into a solid mass, even though it requires temperatures above the melting point for complete conversion to the nitride.

PROPERTIES:

Gray-black; quite stable in air. d (x-ray) 6.40. Crystal structure: type $D5_3$ (Mn_2O_3 type).

REFERENCE:

R. Juza, A Neuber and H. Hahn. Z. anorg. allg. Chem. 239, 273 (1938).

Zinc Phosphides

Zn_3P_2, ZnP_2

$$\underset{196.1}{3\,Zn} + \underset{62.0}{2\,P} = \underset{258.1}{Zn_3P_2} \qquad \underset{65.4}{Zn} + \underset{62.0}{2\,P} = \underset{127.3}{ZnP_2}$$

I. Weighed quantities of zinc and a very slight excess of red phosphorus (total about 12 g.) are slowly heated to 700°C in an evacuated quartz tube, about 12 cm. long and 10-12 mm. I.D.,

placed in an electric furnace. One end of the tube is allowed to project from the furnace to condense the volatilized phosphorus, which when liquid reacts very rapidly with the zinc. The Zn_3P_2 is then heated to 850°C, sublimed to the other end of the tube, which is maintained at 760°C, and kept at this temperature for about one day. A dense, homogeneous sublimate is obtained.

II. A mixture of Zn_3P_2 and ZnP_2 is obtained by passing phosphorus vapor over hot zinc (the procedure is outlined in the case of Zn_3As_2, method I; see p. 1083).

PROPERTIES:

Zn_3P_2: Gray. d (x-ray) 4.54. Evolves PH_3 with acids. Crystal structure: tetragonal, type $D5_9$ (Zn_3P_2 type).

ZnP_2: Orange to red needles. d (x-ray) 3.51. Sublimes without decomposition in an atmosphere containing phosphorus vapor; insoluble in nonoxidizing acids. Crystal structure: tetragonal; space group D_4^4 or D_4^8.

REFERENCES:

I. R. Juza and K. Bär. Z. anorg. allg. Chem. 283, 230 (1956).
II. M. von Stackelberg and R. Paulus. Z. phys. Chem. (B) 28, 427 (1935).

DropBooks

Zinc Phosphate

$$Zn_3(PO_4)_2 \cdot 4\,H_2O$$

I.
$$\underset{862.7}{3\,ZnSO_4 \cdot 7\,H_2O} + \underset{358.0}{2\,Na_2HPO_4 \cdot 2\,H_2O} = \underset{458.2}{Zn_3(PO_4)_2 \cdot 4\,H_2O} + \underset{284.1}{2\,Na_2SO_4} + \underset{98.1}{H_2SO_4} + 21\,H_2O$$

A solution of 5.8 g. of $ZnSO_4 \cdot 7H_2O$ in 400 ml. of H_2O is stirred at the boiling point with a solution of 2.5 g. of $Na_2HPO_4 \cdot 2H_2O$ in 100 ml. of H_2O. The crystalline precipitate which forms immediately is analytically pure.

II.
$$\underset{244.1}{3\,ZnO} + \underset{196.0}{2\,H_3PO_4} + \underset{18.0}{H_2O} = \underset{458.2}{Zn_3(PO_4)_2 \cdot 4\,H_2O}$$

A 69% solution of H_3PO_4 (d 1.52, 100 g.) is saturated at the boiling point (121°C) with ZnO (about 42 g.), taking care to replenish the evaporated water. The solution is then cooled to room

temperature and finally placed in ice. Ten parts (by volume) of ice-cold water is added with vigorous stirring and the solution is filtered into a porcelain dish, in which it is heated (with stirring) on a steam bath. The transparent lamellae of the tetrahydrate precipitate after a short time; they are suction-filtered, washed with boiling water, and dried on a clay plate. Yield 16 g.

PROPERTIES:

Colorless crystals, needle-shaped and tabular. Solubility in H_2O decreases with increasing temperature; can be recrystallized only from solutions containing phosphoric acid. Soluble in dilute acids and dilute ammonia. Loses two moles of H_2O at 100°C, a third mole at 190°C; the anhydrous salt is obtained at about 250°C. d 3.109. Hardness 2–3. Crystal structure: orthorhombic.

SYNONYM:

Zinc orthophosphate.

REFERENCES:

I. E. Thilo and J. Schulz, Z. anorg. allg. Chem. 265, 201 (1951).
II. N. E. Eberly, C. V. Gross and W. S. Crowell, J. Amer. Chem. Soc. 42, 1432 (1920).

Zinc Hydroxyphosphate

$$Zn_2(OH)PO_4$$

$$\underset{4\,H_2O}{Zn_3(PO_4)_2} + ZnO + H_2O = 2\,Zn_2(OH)PO_4$$

458.2 81.4 18.0 485.5

An intimate mixture of 1.146 g. (0.0025 mole) of $Zn_3(PO_4)_2 \cdot 4H_2O$ (cf. p. 1081) and 1.63 g. (0.02 mole) of ZnO is placed in a porcelain crucible and covered with water; the crucible is half full at this point. The crucible is heated in an autoclave for seven hours at 190°C and 12 atm. The product is digested with 8% methanolic acetic acid on a fritted glass filter and is then washed until the filtrate is free of Zn. After drying at 100°C, the product is analytically pure.

PROPERTIES:

Formula weight 242.75. The colorless crystals are identical with the mineral tarbutite. The water of hydration is given off above 450°C. Crystal structure: triclinic.

REFERENCE:

E. Thilo and I. Schulz. Z. anorg. allg. Chem. 265, 201 (1951).

Zinc Arsenides

Zn_3As_2, $ZnAs_2$

$$\underset{196.1}{3\,Zn} + \underset{149.8}{2\,As} = \underset{348.0}{Zn_3As_2} \qquad \underset{65.4}{Zn} + \underset{149.8}{2\,As} = \underset{215.2}{ZnAs_2}$$

I. A Vycor tube containing a porcelain boat with pure zinc is heated to 700°C in an electrical furnace; the atmosphere in the tube consists of dry, pure N_2 or H_2. The As, in a second porcelain boat, is placed at the end of the tube which projects out of the furnace and is heated with a gas flame. The As vapor thus produced is carried over the metal by the stream of N_2 or H_2. Since the metal has already an appreciable vapor pressure at 700°C, crystals of Zn_3As_2 form on the boat rim and on the tube wall, while the unevaporated metal in the boat is converted to a gray-black mass of arsenide.

II. Heating stoichiometric quantities of Zn and As in an evacuated, sealed Vycor bomb at 780°C yields Zn_3As_2. The same conditions will produce $ZnAs_2$, provided an excess of As is used, since the vapor pressure of As in $ZnAs_2$, which results in decomposition of the latter, is quite high at the above temperature.

DropBooks

PROPERTIES:

Zn_3As_2: Gray. Gives off AsH_3 with acids. M.p. 1015°C; d (x-ray) 5.62. Sublimes at the m.p. to give needles or lamellae. Possesses metal-type conductivity. Hardness 3. Crystal structure: type $D5_9$ (Zn_3P_2 type).

$ZnAs_2$: Gray black. Orthorhombic crystals. M.p. 771°C. Sublimes at the m.p. Hardness 3. d (x-ray) 5.08.

REFERENCES:

M. von Stackelberg and R. Paulus. Z. phys. Chem. (B) 28, 427 (1935); W. Heike. Z. anorg. allg. Chem. 118, 264 (1921).

Zinc Thioantimonate

$Zn_3(SbS_4)_2$

$$\underset{408.9}{3\,ZnCl_2} + \underset{962.3}{2\,Na_3SbS_4 \cdot 9\,H_2O} = \underset{696.1}{Zn_3(SbS_4)_2} + \underset{350.7}{6\,NaCl} + \underset{324.3}{18\,H_2O}$$

A solution of 25 g. of Schlippe's salt (see p. 619) in 75 ml. of H_2O is treated with a solution of 10.6 g. of $ZnCl_2$ (or 22.5 g. of

$ZnSO_4 \cdot 7H_2O$) in 50 ml. of H_2O. The chrome yellow precipitate is washed several times by centrifugation with hot water. It is dried at 80°C, then at 100°C; the orange product is ground. It contains about 6% free S, which is extracted in a Soxhlet apparatus with CS_2.

PROPERTIES:

Orange powder. Decomposed by HCl. Discolors at 160°C; loses S at 200°C, forming Sb_2S_3. The corresponding Cd salt is orange-red, the mercury (II) salt ocher yellow. d (pycn.) 3.76.

REFERENCE:

F. Kirchhof, Z. anorg. allg. Chem. 112, 67 (1920).

Diethylzinc

$Zn(C_2H_5)_2$

$$Zn + C_2H_5I = C_2H_5ZnI \qquad 2\,C_2H_5ZnI = Zn(C_2H_5)_2 + ZnI_2$$
$$65.4 \quad 156.0 \quad 221.4 \qquad 442.7 \quad 123.5 \quad 319.2$$

I. The 500-ml. flask *a* of Fig. 282 is charged with 200 g. of dry C_2H_5I (prepared by heating C_2H_5I with Na chips, and siphoning off and distilling the liquid) and 200 g. of zinc dust, previously cleaned with acid and dried at 160–180°C in a stream of CO_2. Dry zinc turnings are then added until the pile of metal projects above the surface of the liquid. A stream of dry, air-free CO_2 or N_2 is introduced through *b*, expelling the air in the system. When the apparatus is filled with inert gas, the tip of tube *c* is dipped slightly into the mercury in cylinder *d* and capillary *b* is rapidly flame-sealed. The flask is then heated in an 80°C water bath. The temperature of the bath is gradually raised to 96°C, while the tip of *c* is lowered into the mercury until it reaches about 20 cm. below the level of the metal. If all necessary precautions to exclude moisture have been taken, the reaction starts after about 1–1.5 hours of refluxing.

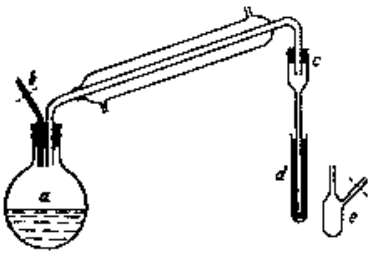

Fig. 282. Preparation of diethylzinc. *d* mercury seal; *e* ampoule for product storage.

The reaction is complete after an additional 1.5–2 hours, when no further droplets of C_2H_5I condense in the flask (solid C_2H_5ZnI). The sealed capillary *b* is cut open, *d* is removed and replaced by vessel *e*, and a slow stream of the inert gas is passed through the system. The flask is then tilted so that the condenser points downward, and the $Zn(C_2H_5)_2$ is distilled on an oil bath (about 200°C) into *e*, which is then sealed in the usual way. Yield about 92%.

II. In Dennis's procedure, the starting material is a zinc–copper compound prepared by reducing a mixture of 200 g. of Zn dust and 25 g. of finely powdered CuO for 20 minutes at 400°C in a stream of H_2; the product must be used immediately. Sufficient contact area between the metal and the C_2H_5I is achieved by mixing the finely ground metal with an equal amount of dry sand.

III. Larger quantities of $Zn(C_2H_5)_2$ may be prepared starting from a zinc alloy containing 5–8% Cu, which is prepared by fusing Zn with brass, casting into rods and cutting into chips. When this alloy is used, one half the necessary quantity of the quite expensive C_2H_5I may be replaced by C_2H_5Br. The reaction is then less vigorous.

The product $Zn(C_2H_5)_2$ is freed of ethane and C_2H_5I by low-pressure fractional distillation. It is stored in sealed ampoules or in a flask provided with a well-greased stopcock.

The same procedure may be used for the preparation of: di-n-propylzinc, b.p. (9 mm.) 40°C; di-n-butylzinc, b.p. (9 mm.), 81°C; and diisopentylzinc, b.p. (12 mm.) 100–103°C.

DropBooks

PROPERTIES:

Colorless liquid. M.p. −30°C, b.p. (760 mm.) 117.6°C, (30 mm.) 27°C, (4 mm.) 0°C; d (20°C) 1.207, (8°C) 1.245. Resistant to CO_2; ignites in air. Decomposes extremely violently in H_2O, forming $Zn(OH)_2$ and C_2H_6. Soluble in ether.

REFERENCES:

I. E. Krause and A. von Grosse. Chemie d. metallorgan. Verbindungen [Chemistry of Organometallic Compounds], Berlin, 1937 [preparative directions cited from Simonovich. Zh. Russ. Fiz.-Khim. Obsch. 31, 38 (1899)].

II. L. M. Dennis. Z. anorg. allg. Chem. 174, 133 (1928).

III. Organic Syntheses. Coll. Vol. 2, New York and London 1943/50, p. 184; H. Grubitsch. Anorgan.-präp. Chemie [Preparative Inorganic Chemistry], Springer, Vienna, 1950, p. 458; A. W. Laubengayer and R. H. Fleckenstein. Z. anorg. allg. Chem. 191, 283 (1930).

Zinc Carbonate

$ZnCO_3$

I. $ZnSO_4 + 4\,KHCO_3 = ZnCO_3 + K_2SO_4 + K_2CO_3 + 2\,CO_2 + 2\,H_2O$

(7 H_2O) 287.6 400.5 125.4 174.3 138.2

Neutral $ZnCO_3$ is obtained when zinc carbonate, precipitated at as low a temperature as possible, is allowed to age for a long time at low, gradually increasing temperature in a CO_2-free atmosphere.

A 1N $KHCO_3$ solution (300 ml.), cooled to 3°C and saturated with CO_2, is added with stirring to 700 ml. of a 0.1M $ZnSO_4$ solution at the same temperature. The temperature is maintained below 10°C during the first 3–4 days; it is then raised to 20°C and maintained there for an additional 2–3 days until the initial flaky precipitate has been transformed into a finely crystalline deposit. The product is washed several times by decantation with water, taking care to remove the flocculent material floating in the supernatant liquor, and washed free of sulfate on a filter. It is dried in a desiccator at room temperature, or by heating at 130°C.

The x-ray powder pattern of the product heated at 130°C corresponds to that of natural smithsonite ($ZnCO_3$), but contains seven additional lines. The yield is satisfactory.

II. $ZnCl_2 + 4\,KHCO_3 + x\,CO_2$

136.3 400.5

$= ZnCO_3 + 2\,KCl + K_2CO_3 + (x+2)\,CO_2 + 2\,H_2O$

125.4 149.1 138.2

Preparation by rapid aging at moderate temperature under CO_2 pressure: 10 ml. of a conc. solution of $ZnCl_2$ is frozen with Dry Ice in a freezing tube. A fourfold excess of solid $KHCO_3$ and 10 ml. of H_2O are added. A few pieces of Dry Ice are added on top and the tube is melt-sealed while still cold. It is kept at room temperature until the contents melt. The tube is then held at 130°C for two hours.

Departures from the above two procedures result in basic products.

PROPERTIES:

Colorless. Converts to the basic salt on boiling with water. **Thermal decomposition** begins at 140°C; at 295.5°C the pressure of CO_2 is 700 mm. Solubility $5.7 \cdot 10^{-5}$ g./100 ml. H_2O. Readily

soluble in acids. d (pycn.) 4.4; d (x-ray) 4.51. Hardness 5 (natural zincspar). Crystal structure: rhombohedral, type $G0_1$ (calcite type).

REFERENCE:

G. F. Hüttig, A. Zörner and O. Hnevkovsky. Monatsh. Chem. 72, 31 (1939).

Zinc Acetate

$Zn(CH_3COO)_2$

$$\underset{297.5}{Zn(NO_3)_2 \cdot 6\,H_2O} + \underset{102.1}{(CH_3CO)_2O} = \underset{183.5}{Zn(CH_3COO)_2} + \underset{126.0}{2\,HNO_3} + \underset{90.1}{5\,H_2O}$$

A mixture of 10.2 g. of $Zn(NO_3)_2 \cdot 6H_2O$ and 40 ml. of acetic anhydride is heated. When the vigorous reaction ceases, the mixture is stored in the cold for some time; the crystal slurry is then suction-filtered, washed with some acetic anhydride and ether, and dried in vacuum over KOH and H_2SO_4. Yield 95%.

PROPERTIES:

Colorless, hexagonal, prismatic crystals. M.p. 242 °C. Sublimes in vacuum without decomposition at lower temperatures; decomposes at temperatures higher than the m.p. d 1.84. Sparingly soluble in cold water, dissolves slowly in warm water. The dihydrate crystallizes from dilute acetic acid, the monohydrate from water and absolute alcohol.

REFERENCE:

E. Späth. Monatsh. Chem. 33, 240 (1912).

Zinc Cyanide

$Zn(CN)_2$

I.
$$\underset{\substack{(7\,H_2O)\\287.6}}{ZnSO_4} + \underset{130.2}{2\,KCN} = \underset{117.4}{Zn(CN)_2} + \underset{174.3}{K_2SO_4}$$

A solution of 10 g. of $ZnSO_4 \cdot 7H_2O$ in 100 ml. of H_2O is mixed (constant stirring) with a KCN solution until no further precipitate is formed (about 5 g. of KCN in 50 ml. of H_2O is needed). The

precipitate, which settles well on prolonged boiling, is washed repeatedly with hot H_2O and dried either with alcohol and ether or at 70°C. Yield about 4 g.

II. $$\underset{183.5}{Zn(CH_3COO)_2} + \underset{54.1}{2\,HCN} = \underset{117.4}{Zn(CN)_2} + \underset{120.1}{2\,CH_3COOH}$$

The $Zn(CN)_2$ is precipitated with hydrocyanic acid from a solution of $Zn(OH)_2$ in CH_3COOH. After washing, the product is dried at 110°C.

PROPERTIES:

White, amorphous powder or shiny, rhombic prisms. Insoluble in H_2O and alcohol. Soluble in alkali cyanides and aqueous ammonia; soluble in dilute acids (evolution of HCN). Decomposes at 800°C; d 1.852. Crystal structure: type C3 (Cu_2O type).

REFERENCES:

I. Ullmann. Enzyklopädie d. techn. Chem. [Encyclopedia of Ind. Chem.], 2nd ed., 10, 718; Loebe. Thesis, Berlin, 1902.
II. W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).

Potassium Tetracyanozincate

$K_2Zn(CN)_4$

I. $$\underset{117.4}{Zn(CN)_2} + \underset{130.2}{2\,KCN} = \underset{247.7}{K_2Zn(CN)_4}$$

Zinc cyanide is dissolved in the equivalent amount of KCN solution. About 10 min. is required at room temperature; the process may be accelerated by heating. The salt precipitates from the solution on concentrating.

II. $$\underset{81.4}{ZnO} + \underset{138.2}{K_2CO_3} + \underset{108.1}{4\,HCN} = \underset{247.7}{K_2Zn(CN)_4} + \underset{44.0}{CO_2} + 2\,H_2O$$

Zinc oxide is suspended in an aqueous solution of the equivalent quantity of K_2CO_3 and treated for several days with gaseous HCN until completely dissolved. Small crystals of the salt complex precipitate from the concentrated filtrate. They are dried at 105°C.

SYNONYM:

Potassium zinc cyanide, zinc potassium cyanide.

PROPERTIES:

Transparent octahedra. M.p. 538°C; d 1.647. Solubility (20°C) 11 g./100 ml. H_2O, 1 g./210 g. of 88% v./v. alcohol. Readily soluble in liquid NH_3. Crystal structure: type B1 (spinel).

REFERENCES:

I. F. Spitzer. Z. Elektrochem. 11, 347 (1905).
II. W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).

Zinc Silicate

Zn_2SiO_4

$$\underset{162.8}{2\,ZnO} + \underset{60.1}{SiO_2} = \underset{222.8}{Zn_2SiO_4}$$

I. Two moles of ZnO and one mole of SiO_2 are intimately mixed. The reaction is facilitated by using finely divided starting materials and compressing the mixed powder into 5-g. tablets. The mixture is placed in a platinum boat inside a ceramic protective tube and heated above the melting point of Zn_2SiO_4 (> 1512°C) in a Tammann furnace. The protective tube is closed at one end, which helps to exclude the reducing furnace gases to some extent. The reaction may be observed through a port made of cobalt glass. The melting point is reached when the upright raw material tablet collapses. To prevent evaporation of the ZnO, the heating must be rapid.

II. Tablets made of a mixture of two moles of Zno and one mole of amorphous SiO_2 are heated for four days between 900 and 1000°C. The x-ray powder pattern of the resultant product indicates a homogeneous material.

III. Pneumatolytic-hydrothermal synthesis from ZnO and ZrO_2 in an autoclave at 365°C.

SYNONYM:

Zinc orthosilicate.

PROPERTIES:

Colorless. Soluble in 20% HF, decomposed by HCl. M.p. 1512°C; d 4.103. Hardness 5.5; crystal structure: type $S1_3$ (Be_2SiO_4 type). At 1432°C. forms a eutectic containing one mole of SiO_2. Phosphoresces on activation with manganese.

REFERENCES:

I. W. Biltz and A. Lemke. Z. anorg. allg. Chem. 203, 330 (1932).
II. A. Pabst. Z. phys. Chem. (A) 142, 227 (1929).
III. C. J. van Nieuwenburg and H. B. Blumendahl. Rec. Trav. Chim. Pays-Bas 50, 129 (1931).

Zinc Fluorosilicate

$ZnSiF_6 \cdot 6H_2O$

$$\underset{81.4}{ZnO} + \underset{144.1}{H_2SiF_6} + \underset{90.1}{5H_2O} = \underset{315.5}{ZnSiF_6 \cdot 6H_2O}$$

Somewhat less than the stoichiometric quantity of ZnO is dissolved in aqueous H_2SiF_6. Complete saturation is avoided because it produces hydrolysis with formation of colloidal silicic acid. The mixture is evaporated on a steam bath in a platinum or lead dish until a film forms on the surface; the film is redissolved with some water and the product is allowed to crystallize over H_2SO_4 in a desiccator.

SYNONYM:

Zinc fluosilicate.

PROPERTIES:

Colorless, rhombohedral prisms, stable in air. Solubility (0°C) 50.3 g. of the anhydrous salt, (10°C) 52.8 g./100 ml. of saturated solution. A saturated solution at 20°C has d ~ 1.4. d (pycn.) 2.139, d (x-ray) 2.15. Crystal structure: trigonal.

REFERENCES:

W. Stortenbecker. Z. phys. Chem. (A) 67, 621 (1909); O. Ruff, C. Friedrich and E. Ascher. Angew. Chem. 43, 1081 (1930).

Zinc Ferrate (III)

$ZnFe_2O_4$

I. $$\underset{81.4}{ZnO} + \underset{159.7}{Fe_2O_3} = \underset{241.1}{ZnFe_2O_4}$$

I. Zinc oxide, precipitated from $ZnCl_2$ solution and dried in vacuum over P_2O_5, is mixed with α- or γ-FeOOH in a ratio of

$1ZnO:1Fe_2O_3$, taking into account the water content. The mixture is then screened and weighed out. The powder is mixed for four hours in a Pyrex bottle on a mechanical shaker. Following this, 4-g. portions of the mixture are placed in an open platinum crucible, which is then set in an electric furnace. The reaction may be carried out either at 800°C in a stream of dry air or at 1000°C in the absence of such an air flow. In either case, one hour is required for the reaction.

When ZnO (prepared by heating $ZnCO_3$ for two hours at 1000°C) and Fe_2O_3 are used instead of the above-specified raw materials, the mixture must be calcined for six hours at 800°C to obtain a $ZnFe_2O_4$ with a pure spinel lattice.

II.

$$\underset{136.3}{ZnCl_2} + 3\,NaOH = \underset{139.4}{Na[Zn(OH)_3]} + \underset{116.9}{2\,NaCl}$$

$$\underset{139.4}{Na[Zn(OH)_3]} + \underset{540.6}{2\,FeCl_3 \cdot 6\,H_2O} + \underset{200.0}{5\,NaOH} = \underset{241.1}{ZnFe_2O_4} + \underset{350.7}{6\,NaCl} + 4\,H_2O$$

A solution of 2.4 moles of NaOH in 300 ml. of H_2O is allowed to react with a solution of 0.15 mole of $ZnCl_2$ in 100 ml. of H_2O. The resultant $Na[Zn(OH)_3]$ solution is treated with a solution of 0.3 mole of $FeCl_3 \cdot 6H_2O$ and 1.2 moles of HCl in 5000 ml. of H_2O (vigorous stirring) and, after stirring two hours, heated for 0.5 hour at 60°C. The mixture is allowed to settle and is then allowed to react with 2N NaOH to a permanent red phenolphthalein color. The product is washed by repeated decantation with 2500-ml. portions of H_2O until the supernatant is free of Cl^- (about 15 washings are required), filtered through a sintered glass filter, washed until the solid is free of Cl^-, and dried in a vacuum desiccator over P_2O_5 and solid KOH. The product then consists of almost black, highly lustrous, brittle pieces. These are crushed, sieved through a 0.15-mm. screen, and redried in the desiccator.

After annealing for one hour at 60°C, two spinel interferences are barely recognizable in the x-ray powder pattern. The spinel pattern becomes fully developed after heating to 500°C.

PROPERTIES:

Dry, brown $ZnFe_2O_4$ is paramagnetic when prepared by either the dry or the wet method. It absorbs more than its equivalent of Fe_2O_3 while maintaining its crystal lattice and becomes ferromagnetic. The magnetizability of these products is maximum at about 70 mole% Fe_2O_3. d (x-ray) 5.395. Crystal structure: type $H1_1$ (spinel type).

REFERENCES:

R. Fricke and W. Dürr. Z. Elektrochem. 46, 254 (1939); G. F. Hüttig, M. Ehrenberg and H. Kittel. Z. anorg. allg. Chem. 228, 112 (1936).

Rinmann's Green

A mixture of the carbonates or oxalates of Zn and Co with an equal amount of KCl (e.g., 15 g. of $ZnCO_3$, 3.5 g. of $CoCO_3$, and 18.5 g. of KCl) is heated several hours at high temperature (> 1000°C) in a Pt crucible. (The KCl serves as a flux and mineralizer.) The material should then be cooled under a CO_2 blanket. The reaction is brought to completion by repeating the procedure several times followed by washing. The KCl must be replenished between heatings.

At higher temperatures and on vacuum calcination, the color becomes lighter; it is malachite green in the presence of an excess of Zn, brownish pink with an excess of Cn. Products calcined below 1000°C contain green-black $ZnCn_2O_4$.

Rinmann's green consists of mixed ZnO-CoO crystals; the green, Co-deficient products (up to about 30% Co) consist of a solid solution of CoO in ZnO (wurtzite lattice). The pink, Co-rich preparations (above 70% CoO) are solutions of ZnO in CoO (NaCl lattice). The intermediate region is heterogeneous.

SYNONYMS:

Cobalt green, turquoise green, cinnabar green.

PROPERTIES:

Soluble in weak acids and solutions of $(NH_4)_2CO_3$. d ~ 5.5.

REFERENCES:

J. A. Hedvall. Z. anorg. allg. Chem. 86, 201 (1914); C. Natta and L. Passerini. Gazz. Chim. Ital. 59, 620 (1929).

Cadmium

(needles)

Cd

$$\underset{(^1/_2\,H_2O)}{CdSO_4} = Cd + H_2SO_4 + {}^1/_2O_2$$

256.5 112.4 98.1

Two platinum disk electrodes (diameter 4.5 cm.) are placed one above the other (distance of about 5 cm.) in a vertical glass

cylinder (I.D. 7 cm.). The lower electrode serves as the cathode, the upper as the anode. The electrolyte is a conc. $CdSO_4$ solution slightly acidified with H_2SO_4. The Cd is deposited as a fine crystalline powder on the cathode at a current density of 0.1–0.3 amp./cm.^{2} The electrolysis vessel fills up quite rapidly with the silvery crystal powder. From time to time the loose powder is compressed with a glass rod to prevent establishment of a short circuit with the anode.

When the Cd in the electrolyte is depleted to such an extent that H_2 begins to evolve at the cathode, the solution must be replenished with $CdSO_4$ to avoid formation of a spongy deposit (the latter also appears at excessive current densities).

The compound is used as filler in the Jones reductor.

PROPERTIES:

Silvery-white crystal powder. M.p. 321°C, b.p. 765°C; d 8.642. Bulk density 80%. Solubility (18°C) 5.17 g./100 g. Hg. Soluble in mineral acids. Hardness 2. Electrochemical equivalent 2.097 g.·(amp.-hr.)$^{-1}$. Crystal structure: type A3 (Mg type).

REFERENCES:

F. P. Treadwell. Helv. Chim. Acta 4, 551 (1921); F. P. Treadwell. Lehrbuch d. analyt. Chemie [Analytical Chemistry], Vol. 2, Vienna, 1949, p. 542.

DropBooks

Cadmium Chloride

$CdCl_2$

I. $$\underset{\substack{(4\,H_2O)\\308.5}}{Cd(NO_3)_2} + \underset{72.9}{2\,HCl} = \underset{183.3}{CdCl_2} + \underset{126.0}{2\,HNO_3}$$

Repeated evaporation with very pure conc. hydrochloric acid converts $Cd(NO_3)_2 \cdot 4\,H_2O$ to the chloride. The product is recrystallized twice. Partial dehydration is achieved by storing for a prolonged time in a vacuum desiccator containing fused KOH (which is frequently replaced). Final dehydration is achieved by careful heating of the product in a stream of HCl, distilling twice in the same stream, and finally fusing the distillate under pure N_2.

II. $$\underset{112.4}{Cd} + \underset{72.9}{2\,HCl} = \underset{183.3}{CdCl_2} + \underset{2.0}{H_2}$$

The reaction between Cd and HCl at 450°C is smooth and uniform. The chloride is distilled twice in a stream of HCl and melted under N_2.

III. $$\underset{230.5}{Cd(CH_3COO)_2} + \underset{157.0}{2\,CH_3COCl} = \underset{183.3}{CdCl_2} + \underset{204.2}{2\,(CH_3CO)_2O}$$

A warm solution of about 4 g. of cadmium acetate (dry) in anhydrous acetic acid (or a mixture of the latter with acetic anhydride) is treated with a slight excess of acetyl chloride or with gaseous HCl. The white precipitate which appears immediately is centrifuged off, washed once or twice with dry benzene, and dried at 100–120°C.

Cadmium bromide may be prepared by the same procedure from cadmium acetate and acetyl bromide (or HBr gas).

PROPERTIES:

Colorless rhombohedral leaflets. M.p. 568°C, b.p. 967°C. Solubility (0°C) 90.1 g. (2.5-hydrate), (20°C) 111.4 g. (2.5-hydrate), (100°C) 150 g. (1-hydrate)/100 ml. H_2O. Crystallizes as the monohydrate above 34°C. Solubility (15.5°C) 1.7 g. of anhydrous $CdCl_2$ per 100 g. of ethanol or methanol. d 4.047. Crystal structure: type C 19 ($CdCl_2$ type). Method III yields a white, microcrystalline powder which in the cold tends to form gelatinous inclusion products with various solvents (e.g., benzene).

REFERENCES:

O. Hönigschmid and R. Schlee. Z. anorg. allg. Chem. 227, 184 (1936); H. D. Hardt. Private communication; A. R. Pray. Inorg. Syn. 5, 153 (1957); E. R. Epperson et al. Ibid. 7, 163 (1963).

Cadmium Hydroxychloride

Cd(OH)Cl

Of the five basic cadmium chlorides, Cd(OH)Cl has the highest chloride content; it is the stable end product of the hydrolysis of not too dilute solutions of $CdCl_2$.

L $$\underset{183.3}{CdCl_2} + \underset{40.0}{NaOH} = \underset{164.9}{Cd(OH)Cl} + \underset{58.5}{NaCl}$$

A 0.1–1M solution of $CdCl_2$ is treated with 30% of the stoichiometric quantity of aqueous NaOH. The resultant solution should have a pH of 6.6. The precipitate is a labile basic chloride which is converted in stages over a period of a few days to the stable Cd(OH)Cl, provided it is in contact with the mother liquor. The theoretical composition is obtained when a 1M solution of $CdCl_2$ is used as the starting material.

II. $$\underset{128.4}{CdO} + \underset{183.3}{CdCl_2} + \underset{18.0}{H_2O} = 2\,\underset{329.8}{Cd(OH)Cl}$$

Cadmium oxide is heated for several days at 210°C with a solution of $CdCl_2$ in a sealed tube.

SYNONYM:

Cadmium chloride hydroxide.

PROPERTIES:

Colorless, elongated, hexagonal prisms. d 4.57. Layer lattice, type $E0_3$ [Cd(OH)Cl type].

REFERENCES:

I. W. Feitknecht and W. Gerber. Helv. Chim. Acta 20, 1344 (1937); Z. Kristallogr. (A) 98, 168 (1937).
II. I. L. Hoard and O. D. Grenko. Z. Kristallogr. (A) 87, 110 (1934).

DropBooks

Potassium Cadmium Chloride

$CdCl_2 \cdot KCl \cdot H_2O$

$$\underset{183.3}{CdCl_2} + \underset{74.6}{KCl} + \underset{18.0}{H_2O} = \underset{275.9}{CdCl_2 \cdot KCl \cdot H_2O}$$

This double salt crystallizes below 36.5°C from an aqueous solution of equimolar quantities of the components. The anhydrous salt crystallizes at higher temperature.

The compound is used in the Lipscomb–Hulett standard cell (704 mv.).

PROPERTIES:

Fine silky needles. The saturated solution contains the following amounts of the anhydrous salt: (2.6°C) 21.87 g., (19.3°C) 27.50 g., (41.5°C) 35.66 g., (105.1°C) 51.67 g./100 g.

REFERENCE:

H. Hering. Comptes Rendus Hebd. Séances Acad. Sci. 194, 1167 (1932).

Cadmium Bromide

$CdBr_2$

$$Cd + Br_2 = CdBr_2$$
$$112.4 \quad 159.8 \quad 272.2$$

Cadmium is brominated at 450°C in a quartz boat placed inside a Vycor tube initially filled with dry N_2. Nitrogen is then passed through a washing bottle filled with Br_2 and introduced into the tube. The complete bromination of 3 g. of Cd requires about two hours at 450°C. Raising the temperature to increase the reaction rate is not recommended, since this may cause appreciable quantities of the metal to distill with the product. The molten $CdBr_2$ is deep red as long as unreacted metal is present and becomes increasingly lighter as the metal is consumed, so that the end of the reaction may be readily recognized by the final permanent light color. The product $CdBr_2$ is distilled twice in a stream of Br_2 by raising the temperature; it is freed of excess Br_2 by remelting under pure CO_2. The entire procedure may be carried out in the apparatus described by O. Hönigschmid and F. Wittner [Z. anorg. allg. Chem. 226, 297 (1936)] for the preparation of pure uranium halides; it is also described under UBr_4 (p. 1440).

Alternate method: See under zinc chloride (p. 1070) and cadmium chloride (p. 1093).

PROPERTIES:

Colorless, hexagonal, pearly flakes; highly hygroscopic. M.p. 566°C, b.p. 963°C; d 5.192. Solubility (18°C) 95 g., (100°C) 160 g. per 100 ml. H_2O. Crystallizes as the monohydrate below 36°C, as the tetrahydrate above this temperature. Solubility (15°C) 26.4 g. of anhydrous $CdBr_2$/100 g. alcohol. Crystal structure: type C 19 ($CdCl_2$ type).

REFERENCE:

O. Hönigschmid and R. Schlee. Z. anorg. allg. Chem. 227, 184 (1936).

Cadmium Iodide

CdI_2

$$Cd + I_2 = CdI_2$$
$$112.4 \quad 253.8 \quad 366.3$$

Cadmium shavings (or Cd slurry obtained from $CdSO_4$ solution + Zn) are shaken in distilled H_2O with the equivalent quantity

of resublimed iodine. The shaking may be dispensed with if the mixture is refluxed for two hours. After the color of the liquid disappears, it is filtered and concentrated on a steam bath. The crystals are vacuum-dried for 24 hours over P_2O_5 at 100–150°C.

Carefully dried CdI_2 may be sublimed in a stream of oxygen-free CO_2. The CdI_2 vapor is condensed in a long glass tube closed off with canvas. This yields "CdI_2 flowers."

II.

$$\underset{(^5/_2\ H_2O)\ 256.5}{CdSO_4} + \underset{332.0}{2\,KI} = \underset{366.3}{CdI_2} + \underset{174.3}{K_2SO_4}$$

An aqueous solution of three parts of $CdSO_4 \cdot 8/3\ H_2O$ and four parts of KI is evaporated to dryness and extracted with warm absolute alcohol. The CdI_2 crystallizes in colorless lamellae upon cooling of the solution.

Alternate method: See under zinc chloride, p. 1070.

PROPERTIES:

Colorless, lustrous, hexagonal leaflets; stable in air. M.p. 387°C, b.p. 787°C; d 5.67. Solubility (18°C) 85 g., (100°C) 128 g./100 ml. H_2O; (20°C) 176 g./100 ml. methanol; ~90 g./100 ml. of ethanol. Soluble in ether. Crystal structure: type C 6 (CdI_2) and C27 (second CdI_2 type). d (x-ray) of both structures is identical.

DropBooks

REFERENCES:

I. W. Biltz and C. Mau. Z. anorg. allg. Chem. 148, 170 (1925); E. Cohen and A. L. Th. Moesveld. Z. phys. Chem. 94, 471 (1920).
II. Jahresber. Fortschr. d. Chem. 1864, 242.

Cadmium Hydroxide

$Cd(OH)_2$

I. COARSE CRYSTALS

$$\underset{366.3}{CdI_2} + \underset{112.2}{2\,KOH} = \underset{146.4}{Cd(OH)_2} + \underset{332.0}{2\,KI}$$

A solution of 10 g. of CdI_2 in 200 ml. of water is mixed with 320 g. of carbonate-free KOH. The mixture is heated until the first precipitate of $Cd(OH)_2$ redissolves at about 135°C. The heating must be accompanied by continuous stirring to prevent

the lower layers of the liquid from reaching a temperature high enough to cause partial conversion of the $Cd(OH)_2$ to black, sparingly soluble CdO. The major part of the $Cd(OH)_2$ crystallizes when the solution is slowly cooled. However, a part of the hydrate remains in solution even after complete cooling and may precipitate as amorphous $Cd(OH)_2$ if the product is immediately treated with water. Therefore, the mixture is allowed to stand for 12 hours before attempting to separate the $Cd(OH)_2$ with water.

II. Very homogenous $Cd(OH)_2$ is obtained from cadmium acetate and 85% KOH following precipitation of crystalline CdO by the same procedure.

III. *FINE CRYSTALS*

$$\underset{308.5}{Cd(NO_3)_2 \cdot 4H_2O} + \underset{80.0}{2\,NaOH} = \underset{146.4}{Cd(OH)_2} + \underset{170.0}{2\,NaNO_3} + 5\,H_2O$$

A finely crystalline product is obtained by dropwise addition (stirring or shaking) of a boiling solution of $Cd(NO_3)_2$ to boiling, carbonate-free 0.82N NaOH (stoichiometric quantities). The precipitate is repeatedly washed with hot water and vacuum-dried over P_2O_5 at 60°C. (For details, see in the original.)

PROPERTIES:

Nacreous, hexagonal leaflets soluble in acids and NH_4Cl solution. Solubility (25°C) 0.26 mg./100 ml. H_2O; 0.13 g./100 ml. 5N NaOH. Dehydration starts at 130°C, is complete at 200°C. d 4.79. Crystal structure: type C6 (CdI_2 type).

REFERENCES:

I. A. de Schulten. Comptes Rendus Hebd. Séances Acad. Sci. 101, 72 (1885).
II. R. Scholder and E. Staufenbiel. Z. anorg. allg. Chem. 247, 271 (1941).
III. R. Fricke and F. Blaschke. Z. Elektrochem. 46, 46 (1940).

Cadmium Sulfide

CdS

$$\underset{(^1/_2\,H_2O)\ 250.5}{CdSO_4} + \underset{22.4\,l.}{H_2S} = \underset{144.5}{CdS} + \underset{98.1}{H_2SO_4}$$

Finely divided cubic CdS is obtained by precipitation with H_2S of a hot, H_2SO_4-acidified aqueous solution of $CdSO_4$. The hexagonal

modification (more or less free of cubic CdS) is obtained from cadmium halide solutions; however, the resultant sulfide is contaminated with strongly adhering halide which cannot be washed out.

Depending on the particle size and the state of the surface, the color of the precipitates varies from lemon yellow to orange. Lemon yellow "cadmium yellow" is prepared by precipitating, with constant stirring, a very diluted neutral solution of $CdSO_4$ with an excess of Na_2S solution. The precipitate is then washed free of sulfate.

Dark CdS is obtained by calcining a mixture of two parts of $CdCO_3$ and one part of sulfur powder in a crucible. The product is pulverized after cooling.

Pure CdS, free of the anions of the precipitating medium, is prepared by bubbling H_2S through a solution of $Cd(ClO_4)_2$ in 0.1–0.3N perchloric acid. Lower acid concentrations yield precipitates which are difficult to filter; the precipitation is incomplete at higher concentrations.

Crystals a few millimeters in size are obtained from H_2S and Cd vapor at about 800°C (see Frerichs' method in the literature below).

PROPERTIES:

Lemon-yellow to orange powder. Solubility (18°C) 0.13 mg./100 ml. H_2O. Soluble in conc. or warm dilute mineral acids. Sublimes at 980°C. d 4.82. Hardness 3. Crystal structure: cubic type B 3 (zincblende type) and hexagonal type B 4 (wurtzite type). The cubic modification is converted to the hexagonal by heating at 700–800°C in sulfur vapor.

REFERENCES:

W. O. Milligan. J. Phys. Chem. 38, 797 (1934); H. B. Weiser and E. J. Durham. Ibid. 32, 1061 (1928); W. J. Müller and G. Löffler. Angew. Chem. 46, 538 (1933); E. Dönges. Unpublished; G. Denk and F. Denk. Z. analyt. Chem. 130, 383 (1949/50); R. Frerichs. Naturwiss. 33, 2181 (1946).

CADMIUM SELENIDE CdSe

The preparation is analogous to that of ZnSe (method I, see p. 1078).

PROPERTIES:

Formula weight 191.37. Dark-red powder. d (x-ray) 5.767. Crystal structure: type B 3 (zincblende type) and B 4 (wurzite type).

Cadmium Nitride

Cd_3N_2

$$\underset{433.4}{3\,Cd(NH_2)_2} = \underset{365.3}{Cd_3N_2} + \underset{68.1}{4\,NH_3}$$

Cadmium amide, $Cd(NH_2)_2$, is thermally decomposed in a vapor pressure eudiometer (see Part I, p. 102) at 180°C while repeatedly removing measured amounts of NH_3. The evolution of NH_3 ceases after about 36 hours. The Cd_3N_2 product decomposes if the temperature is raised higher.

PROPERTIES:

Black; forms oxide in air. d (x-ray) 7.67. Crystal structure: type $D5_3$ (Mn_2O_3).

REFERENCE:

H. Hahn and R. Juza, Z. anorg. allg. Chem. 244, 111 (1940).

Cadmium Amide

$Cd(NH_2)_2$

$$\underset{228.6}{Cd(SCN)_2} + \underset{110.2}{2\,KNH_2} = \underset{144.5}{Cd(NH_2)_2} + \underset{194.4}{2\,KSCN}$$

Cadmium thiocyanate (7 g.) is placed on filter disk *b* of vessel *a* (Fig. 283). About 15 ml. of carefully purified NH_3 is condensed

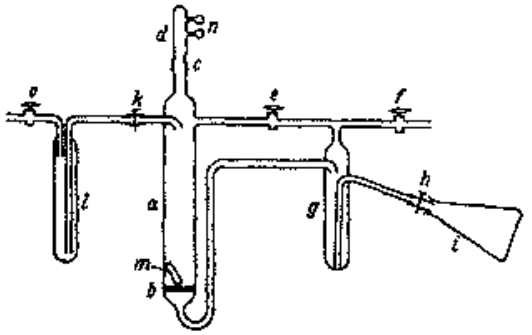

Fig. 283. Preparation of cadmium amide. *h* and *k* pinch clamps; *l* storage vessel for ammonia; *m* glass slug; *n* glass bulbs.

onto the salt, which then dissolves in the ammonia. A solution of KNH_2 in liquid NH_3 is added to the above mixture through the ground joint *c*, and the vessel is closed off with ground cap *d*. A fluffy, white precipitate of $Cd(NH_2)_2$ is formed. The amount of KNH_2 used must be somewhat less than stoichiometric as $Cd(NH_2)_2$ dissolves in excess KNH_2. In addition, no air must be allowed to be present during the reaction; a stream of N_2 is therefore passed through the apparatus when it is opened for any reason.

After thorough mixing of the two solutions, the supernatant liquid containing KSCN and excess $Cd(SCN)_2$ in liquid NH_3 is filtered by suction through disk *b*. This operation is performed by closing stopcock *e* and carefully evacuating the apparatus through *f*; this results in transfer of the liquid from *a* to *g*, which is cooled with Dry Ice-alcohol. The liquid is then removed from the system and into flask *i* by application of slight pressure, achieved by closing *f*, raising the temperature in *g* temporarily (remove the cooling bath), and opening the screw pinchcock *h*. After closing *h*, the product is washed by producing a slight vacuum in the system and transferring fresh liquid ammonia from storage vessel *l* through screw pinchcock *k* onto the product in *a*. Washing is complete when the NH_3 evaporates without leaving a residue. When this point is reached, all the NH_3 is removed (by suction) from the product. The latter is then knocked off the walls by means of the glass slug *m* and transferred to bulbs *n*. The preparation is carried out at (or near) the boiling point of NH_3 (−33.5°C). Very pure N_2, introduced through stopcocks *g* or *f*, is used as the blanketing gas.

PROPERTIES:

Slightly yellowish, amorphous; rapidly discolors to brown in air. d 3.05.

REFERENCE:

R. Juza, K. Fasold and W. Kuhn. Z. anorg. allg. Chem. 234, 86 (1937).

Cadmium Phosphides

Cd_3P_2, CdP_2, CdP_4

I.

$$\underset{337.2}{3\,Cd} + \underset{62.0}{2\,P} = \underset{399.2}{Cd_3P_2}$$

The procedure for the preparation Cd_3P_2 is similar to that for Zn_3P_2 (method I, see p. 1080); that is, it is produced in an

evacuated quartz tube from Cd metal and red P. The temperature along the tube varies from 400 to 600°C. The mixture is allowed to react for about nine hours, and the entire tube is then heated for 12 hours at 680°C. The resultant Cd_3P_2 is resublimed several times over an open flame, and finally sublimed at 680°C into a slightly colder part of the quartz tube.

II. $$\underset{112.4}{Cd} + \underset{62.0}{2P} = \underset{174.4}{CdP_2}$$

A mixture of CdP_2 with Cd_3P_2 is formed by using the procedure given (see p. 1083) for Zn_3As_2 (method I).

III. $$\underset{112.4}{Cd} + \underset{124.0}{4P} = \underset{236.4}{CdP_4}$$

A mixture of 0.6 g. of white phosphorus and 20 g. of a Pb-Cd alloy containing 5% Cd is sealed under a CO_2 blanket in a Vycor ampoule. The ampoule is heated in an electric furnace to 565–575°C (the heatup time is a few hours) and maintained at this temperature for 2.5–5 days. If large crystals are desired, the temperature gradient in the furnace should be small and the cooling slow. The CdP_4 is purified by boiling with glacial acetic acid and H_2O_2 and subsequent treatment with 20% hydrochloric acid.

The starting Pb-Cd alloy is prepared by fusing the two metals under KCN in a porcelain crucible and cutting the product into strips. Commercial phosphorus is purified by melting under dilute chromosulfuric acid and dried under CO_2.

PROPERTIES:

Cd_3P_2: Gray, lustrous needles or leaflets. M.p. 700°C; d (x-ray) 5.60. Soluble in hydrochloric acid with evolution of PH_3, explosive reaction with conc. nitric acid. Crystal structure: tetragonal, type $D5_9$ (Zn_3P_2).

CdP_2: Orange to red [appears occasionally in an indigo blue modification: B. Renault, Comptes Rendus Hebd. Séances Acad. Sci. 76, 283 (1873)]. Tetragonal needles. d (x-ray) 4.19.

CdP_4: Black, highly reflecting crystals. Very unreactive, dissolves in boiling aqua regia. Decomposes into the elements on heating in vacuum. d (pycn.) 3.90. Crystal structure: monoclinic, space group C_{2h}^5.

REFERENCES:

I. R. Juza and K. Bär. Z. anorg. allg. Chem. 283, 230 (1956).
II. M. von Stackelberg and R. Paulus. Z. phys. Chem. (B) 28, 427 (1935).
III. H. Krebs, K. H. Müller and G. Zürm. Z. anorg. allg. Chem. 286, 16 (1956).

Cadmium Arsenides

Cd_3As_2, $CdAs_2$

$$\underset{337.2}{3\,Cd} + \underset{149.8}{2\,As} = \underset{487.1}{Cd_3As_2} \qquad \underset{112.4}{Cd} + \underset{149.8}{2\,As} = \underset{262.2}{CdAs_2}$$

The preparation of Cd_3As_2 is similar to that of Zn_3As_2 (method I): heating the metal in a stream of hydrogen that carries arsenic vapor (see p. 1083).

The phase diagram indicates the existence of $CdAs_2$, which may be prepared by fusing the components.

PROPERTIES:

Cd_3As_2: Gray. M.p. 721°C. Hardness < 3.5. d (x-ray) 6.35, d (pycn.) 6.211. Crystal structure: tetragonal, type $D5_9$ (Zn_3P_2).

$CdAs_2$: Gray-black. M.p. 621°C. Hardness 3.5-4.

REFERENCES:

M. von Stackelberg and R. Paulus. Z. phys. Chem (B) 28, 427 (1935); A. Granger. Comptes Rendus Hebd. Séances Acad. Sci. 138, 674 (1904); Zemczuny. Z. Metallographie 4, 228 (1913).

DropBooks

Diethylcadmium

$Cd(C_2H_5)_2$

$$\underset{109.0}{C_2H_5Br} + \underset{24.3}{Mg} = \underset{133.3}{C_2H_5MgBr}$$

$$\underset{266.6}{2\,C_2H_5MgBr} + \underset{272.2}{CdBr_2} = \underset{141.5}{Cd(C_2H_5)_2} + \underset{368.3}{2\,MgBr_2}$$

Anhydrous, finely ground $CdBr_2$ (136 g., 0.5 mole) is added in small portions (vigorous shaking and no cooling) to a solution of C_2H_5MgBr in 350 ml. of absolute ether. The latter reagent is prepared from 29 g. (1.2 moles) of Mg and 131 g. (1.2 moles) of C_2H_5Br, the amount required to dissolve the metal. The major portion of the ether is distilled off in a stream of N_2 on a water bath whose temperature does not exceed 80°C. The solid, porous, gray mass left in the flask is then distilled at 1 mm. into a liquid-nitrogen-cooled trap, while the temperature of the oil bath is raised from 20 to 120°C over the one-hour distillation period.

The clear, completely colorless distillate is carefully freed of ether by distilling the latter in a nitrogen stream; the residue is distilled in N_2 at 19.5 mm. All the $Cd(C_2H_5)_2$ goes over at 64.0°C; it is analytically pure. Yield 90%.

PROPERTIES:

Colorless oil with an unpleasant odor. M.p. −21°C, b.p. (19.5 mm.) 64°C, (760 mm.) 164.7°C. Decomposes at 150°C, explosively at 180°C. May be stored without decomposition in a sealed tube filled with N_2. Fumes explosively in air, at first forming white and then (rapidly) brown clouds accompanied by violent detonation. Decomposed by H_2O with a characteristic crackling sound continuing for hours on end. d (21.7°C) 1.653.

REFERENCE:

E. Krause. Ber. dtsch. chem. Ges. 50, 1813 (1918).

Cadmium Carbonate

$CdCO_3$

I. $$\underset{183.3}{CdCl_2} + \underset{96.1}{(NH_4)_2CO_3} + \underset{68.1}{4\,NH_3} = \underset{240.5}{[Cd(NH_3)_4]CO_3} + \underset{107.0}{2\,NH_4Cl}$$

$$\underset{240.5}{[Cd(NH_3)_4]CO_3} = \underset{172.4}{CdCO_3} + \underset{68.1}{4\,NH_3}$$

A solution of $(NH_4)_2CO_3$ is added all at once to a solution of $CdCl_2$, followed by the quantity of ammonia necessary to dissolve the resultant precipitate. The liquid is then heated in an open vessel on a water bath. The $CdCO_3$ separates as shiny crystals.

II. $$\underset{183.3}{CdCl_2} + \underset{72.9}{2\,HCl} + \underset{54.1}{3\,H_2O} + \underset{120.1}{2\,CO(NH_2)_2} = \underset{172.4}{CdCO_3} + \underset{214.0}{4\,NH_4Cl} + \underset{44.0}{CO_2}$$

A vertical bomb (wall thickness 3 mm., diameter 25 mm., height about 50 cm.) contains a solution of 10 mmoles of $CdCl_2$ in 30 ml. of H_2O, 0.3 ml. of conc. hydrochloric acid, and a small glass beaker filled with 20 mmoles of urea. A long stem from the bottom of the bomb supports the beaker above the liquid surface. The bomb is melt-sealed and heated at 200°C for 18–24 hours. The yield is almost quantitative.

PROPERTIES:

White powder or rhombohedral leaflets. Sparingly soluble in H_2O, soluble in acid. Vapor pressure at decomposition (321°C) 77 mm., (357°C) 760 mm. d 4.258. Crystal structure: type $CaCO_3$ (calcite).

REFERENCES:

I. A. de Schulten. Bull. Soc. Chim. France [3] 19, 34 (1898).
II. W. Biltz. Z. anorg. allg. Chem. 220, 312 (1934).

Cadmium Acetate

$Cd(CH_3COO)_2$

$$\underset{308.5}{Cd(NO_3)_2 \cdot 4\,H_2O} + \underset{102.1}{(CH_3CO)_2O} = \underset{230.5}{Cd(CH_3COO)_2} + \underset{124.0}{2\,HNO_3} + 3\,H_2O$$

A mixture of 5 g. of $Cd(NO_3)_2 \cdot 4\,H_2O$ and 25 ml. of acetic anhydride is heated; when the vigorous reaction has ceased, the mixture is refluxed 15 minutes. After cooling and suction-filtering, the white, crystalline precipitate is washed with some acetic anhydride and ether, and vacuum-dried over KOH and H_2SO_4. Yield 3.6 g. (97%).

PROPERTIES:

Colorless crystals. M.p. 254–256°C; d 2.341.

REFERENCE:

E. Späth. Monatsh. Chem. 33, 241 (1912).

DropBooks

Cadmium Cyanide

$Cd(CN)_2$

$$\underset{146.4}{Cd(OH)_2} + \underset{54.1}{2\,HCN} = \underset{164.5}{Cd(CN)_2} + \underset{36.0}{2\,H_2O}$$

Evaporation of a solution of $Cd(OH)_2$ in aqueous HCN precipitates $Cd(CN)_2$ in the form of crystals. These are dried at 140°C.

PROPERTIES:

Air-stable crystals; turn brown on heating in air. Solubility (15°C) 1.7 g./100 ml. H_2O. Soluble in KCN solution. d 2.226. Crystal structure: type C 3 (Cu_2O type).

REFERENCE:

W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).

Potassium Tetracyanocadmate

$K_2Cd(CN)_4$

$$\underset{164.4}{Cd(CN)_2} + 2\,\underset{130.2}{KCN} = \underset{294.7}{K_2Cd(CN)_4}$$

Cadmium cyanide, obtained by precipitation of a $CdSO_4$ solution with KCN and filtering, is dissolved (shaking) in an aqueous solution of the stoichiometric quantity of KCN. The filtrate is crystallized by evaporation. The product is dried at 105°C.

SYNONYMS:

Potassium cadmium cyanide, cadmium potassium cyanide.

PROPERTIES:

Octahedral, very refractive, air-stable crystals. Solubility (cold) 33.3 g., (b.p.) 100 g./100 ml. H_2O; (20°C) 2 g./100 g. of 88% v./v. alcohol. M.p. about 450°C; d 1.846. Crystal structure: type $H1_1$ (spinel type).

REFERENCE:

W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).

Cadmium Thiocyanate

$Cd(SCN)_2$

$$\underset{(\frac{8}{3}\,H_2O)\ 258.5}{CdSO_4} + \underset{253.5}{Ba(SCN)_2} = \underset{228.6}{Cd(SCN)_2} + \underset{233.4}{BaSO_4}$$

To a boiling solution of 12.68 g. of $Ba(SCN)_2$ is added, in drops, 12.83 g. of $CdSO_4 \cdot \frac{8}{3}\,H_2O$ in 100 ml. of boiling H_2O, taking care to keep the liquid boiling. After cooling, the precipitate is allowed to settle and the mixture is filtered after standing for some time. The filtrate is evaporated to 80 ml., filtered again, and evaporated to dryness on a water bath.

The required starting solution of $Ba(SCN)_2$ is prepared by dissolving 15.78 g. of $Ba(OH)_2 \cdot 8\,H_2O$ in 500 ml. of H_2O and allowing it to react with a solution of 7.62 g. of NH_4SCN in 100 ml. of H_2O, according to the equation

$$\underset{315.5}{Ba(OH)_2 \cdot 8\,H_2O} + 2\,\underset{152.2}{NH_4SCN} = \underset{253.5}{Ba(SCN)_2} + \underset{34.1}{2\,NH_3} + \underset{180.2}{10\,H_2O}$$

The mixture is brought to a boil and heated until NH_3 ceases to evolve.

SYNONYMS:

Cadmium rhodanide.

PROPERTIES:

Colorless crystal crusts. Soluble in H_2O, alcohol and liquid NH_3.

REFERENCE:

H. Grossmann. Ber. dtsch. chem. Ges. 35, 2666 (1902).

Cadmium Silicate

Cd_2SiO_4

$$\underset{256.8}{2\,CdO} + \underset{60.1}{SiO_2} = \underset{316.9}{Cd_2SiO_4}$$

Like Zn_2SiO_4, Cd_2SiO_4 is prepared from the oxides by fusion or by hydrothermal synthesis (see p. 1089).

DropBooks

SYNONYM:

Cadmium orthosilicate.

PROPERTIES:

M.p. 1246°C; d 5.833. Phosphorescent after activation with manganese.

REFERENCE:

W. Biltz and A. Lemke. Z. anorg. allg. Chem. 203, 330 (1932); C. J. van Nieuwenburg and H. B. Blumendahl. Rec. Trav. Chim. Pays-Bas 50, 989 (1931).

Cadmium Ferrate (III)

$CdFe_2O_4$

$$\underset{172.4}{CdCO_3} + \underset{159.7}{Fe_2O_3} = \underset{288.1}{CdFe_2O_4} + \underset{44.0}{CO_2}$$

Finely screened $CdCO_3$ [or $Cd(OH)_2$] and γ-FeOOH (p. 1500) in a Cd:Fe ratio of 1:2 are mixed for five hours on a mechanical

shaker in an atmosphere free of CO_2 and H_2O. The loose powder is divided into 5-g. portions, which are heated for one hour in a platinum crucible at 800°C [mixtures with $Cd(OH)_2$ at 1000°C] and then allowed to cool to room temperature in a desiccator. The compound cannot be prepared by precipitation.

PROPERTIES:

Dark brown, hygroscopic powder; stable at room temperature. Crystal structure: type $H1_1$ (spinel type).

REFERENCE:

R. Fricke and F. Blaschke, Z. anorg. allg. Chem. 251, 396 (1943).

Mercury (II) Oxychloride

$HgCl_2 \cdot 4\,HgO$

I. To prepare brown $HgCl_2 \cdot 4\,HgO$, a solution of 15.0 g. of borax in 1.5 liters of water is added to a solution of 10.0 g. of mercuric chloride in 2.0 liters of water (both solutions are at 50–55°C). The desired compound separates on cooling in the form of thin, flexible flakes 0.1–0.8 mm. long. Depending on the thickness of these flakes, the color of the precipitate varies from golden yellow to black-brown. The yield is about 85%, based on the $HgCl_2$ used.

II. Black $HgCl_2 \cdot 4\,HgO$ is obtained when 5.0 g. of finely crystalline brown $HgCl_2 \cdot 4\,HgO$ is heated for 72 hours in a sealed tube with 10 ml. of 0.1N HNO_3 at 180°C. The product separates in the form of rhombic needles several millimeters long, which are readily isolated from the basic nitrate present in the mixture.

SYNONYM:

Mercuric oxychloride.

PROPERTIES:

I. Depending on the thickness, golden yellow to dark brown flakes; elongated brown crystals from concentrated solutions. Soluble in hot water (partial decomposition). The powder pattern distinguishes it from the black form (appearance of lattice defects). Brown $HgCl_2 \cdot 4\,HgO$ has a remarkably wide phase range, from 3.82 to 4.00 HgO.

II. Black, needle-shaped crystals, sparingly soluble in water, d (pycn.) 9.01. Crystal structure: orthorhombic, space group D_{2h}^{26}.

REFERENCES:

I. A. Weiss, G. Nagorsen and A. Weiss. Z. Naturforsch. 9b, 81 (1954).
II. A. Weiss. Private communication.

Mercury (II) Bromide

$HgBr_2$

$$\underset{200.6}{Hg} + \underset{159.8}{Br_2} = \underset{360.4}{HgBr_2}$$

Five parts of Hg are covered with 60 parts of H_2O and allowed to react at 50°C (vigorous stirring) with four parts of Br_2, which is added dropwise as long as no permanent color is formed. The solution is then brought to a boil, filtered hot, and placed in an ice bath to induce crystallization. The salt is dried at as low a temperature as possible. Purification is by careful double or triple sublimation from a porcelain dish heated on a sand bath and covered with a Petri dish. When very high purity is required (e.g., for conductivity measurements), it may be necessary to repeat the sublimation several times more.

DropBooks

PROPERTIES:

Colorless, lustrous crystal flakes (sublimate and from H_2O), rhombic prisms or needles (from alcohol). Light yellow liquid between m.p. 238°C and b.p. 320.3°C. d^{20} 5.73; d^{242} (liq.) 5.11. Vapor pressure (200°C) 24.1 mm., (280°C) 334.2 mm.; sublimes without decomposition. Solubility (25°C) 0.62 g., (100°C) 22 g. per 100 g. H_2O; (25°C) 30.0 g./100 g. ethanol; (25°C) 69.4 g./100 g. methanol. Specific electrical conductivity (242°C) $1.45 \cdot 10^{-4}$ ohm^{-1}. Its melt is a solvent for a large number of inorganic and organic substances, which impart considerable conductivity to the melt. Cryoscopic constant 36.7 deg. per mole in 1000 g. of $HgBr_2$. Rhombic layered lattice, space group C_{2v}^{12}.

REFERENCES:

W. Reinders. Z. phys. Chem. (A) 32, 514 (1900); G. Jander and K. Brodersen. Z. anorg. Chem. 261, 264 (1950).

Potassium Triiodomercurate (II)

$KHgI_3 \cdot H_2O$

$$KI + HgI_2 + H_2O = KHgI_3 \cdot H_2O$$
$$166.0 \quad 454.5 \quad 18.0 \quad 638.5$$

First, 41 g. of KI and 59 g. of HgI_2 are dissolved in 14 (!) ml. of hot H_2O. The beaker should be tared precisely so that evaporating H_2O may be replenished. The salt crystallizes in yellow needles from the cooling solution. The above instructions result from a study of the three-component system HgI_2–KI–H_2O showing that in this system only $KHgI_3 \cdot H_2O$ can precipitate. Yield 9 g.

The salt K_2HgI_4 (without water of crystallization) is obtained from acetone containing exactly 2% H_2O (between 34 and 56°C).

Use: A solution treated with KI is known as Thoulet's solution (see Part I, p. 99); it is also a reagent for alkaloids. Alkaline K_2HgI_4 solution is Nessler's reagent.

SYNONYMS:

Mercury potassium iodide, potassium mercuriiodide, potassium iodohydrargyrate.

PROPERTIES:

Light yellow crystal needles; becomes orange-red in a vacuum desiccator over H_2SO_4 (reversible loss of H_2O). Decomposes in H_2O with loss of HgI_2. Soluble in KI solution. Sublimes off HgI_2 on heating.

REFERENCES:

M. Pernot. Comptes Rendus Hebd. Séances Acad. Sci. 182, 1154 (1926); 185, 950 (1927); Ann. Chim. [10] 15, 5 (1931).

Copper (I) Tetraiodomercurate (II)

Cu_2HgI_4

I.
$$2\,CuSO_4 \cdot (5\,H_2O) + K_2HgI_4 + SO_2 + 2\,H_2O$$
$$499.4 \quad 786.5 \quad 64.1 \quad 36.0$$

$$= Cu_2HgI_4 + K_2SO_4 + 2\,H_2SO_4$$
$$835.4 \quad 174.3 \quad 196.2$$

A solution of 4.5 g. of HgI_2 and 3.3 g. of KI in 25 ml. of H_2O is filtered and treated with a solution of 5 g. of $CuSO_4 \cdot 5\,H_2O$ in 15 ml. of H_2O; SO_2 is then introduced. The resultant bright-red

precipitate is suction-filtered, washed with H_2O, and dried at 100°C. The compound may be recrystallized from hot hydrochloric acid.

II.
$$\underset{380.9}{2\,CuI} + \underset{454.5}{HgI_2} = \underset{835.4}{Cu_2HgI_4}$$

The components are mixed in stoichiometric proportions and fused over an open flame in an evacuated Pyrex glass bomb, which should be as small as possible. Pure Cu_2HgI_4 is obtained.

An analogous procedure yields Ag_2HgI_4.

PROPERTIES:

Red crystalline powder or small, tabular crystals, d 6.094. Crystal structure: tetragonal. Space group D_{2d}^{11}; on heating to 70°C, the color changes to chocolate brown with simultaneous enantiotropic structure transformation to cubic type B3 (zinc-blende) in which the cation distribution is random.

REFERENCES:

I. Cabentou and Willm, Bull. Soc. Chem. France [2] 13, 194 (1870); J. A. A. Ketelaar, Z. Kristallogr. 80, 190 (1931).
II. H. Hahn, G. Frank and W. Klingler, Z. anorg. allg. Chem. 279, 271 (1955).

PropBooks

Mercury (II) Sulfide

HgS

BLACK MODIFICATION

$$\underset{271.5}{HgCl_2} + \underset{22.4\,l.}{H_2S} = \underset{232.7}{HgS} + \underset{72.9}{2\,HCl}$$

Hydrogen sulfide is introduced into a mercury (II) solution in 1–2N HCl, absolutely free of oxidizing agents. The transient white to brownish precipitate reacts with additional H_2S to yield black HgS, e.g.,

$$Hg_3S_2Cl_2 + H_2S = 3\,HgS + 2\,HCl.$$

SYNONYMS:

Ethiop's mineral; mercuric sulfide, black.

RED MODIFICATION

$$\underset{318.7}{Hg(CH_3COO)_2} + \underset{22.4\,l.}{H_2S} = \underset{232.7}{HgS} + 2\,\underset{120.1}{CH_3COOH}$$

A solution of 35 g. of $Hg(CH_3COO)_2$ and 25 g. of NH_4SCN in 100 ml. of hot glacial acetic acid is prepared. A moderately fast stream of H_2S is then introduced until precipitation is complete. The acetic acid is then slowly evaporated (caution, HCN!), and the black precipitate transforms to the red form. The glacial acetic acid must be present until conversion is complete; overheating must be avoided. During the last stage the paste must be constantly stirred. If this is neglected, the product is dull red or brown. When the acid has been completely removed and the product cooled, 200 ml. of H_2O is added and the mixture is filtered through a Büchner funnel. The product is washed and dried between two layers of thick filter paper. Yield 25 g.

If $HgCl_2$ is used instead of the acetate, a larger amount of glacial acetic acid is necessary and the boiling must be longer. The final color, however, is never as magnificent as that of the product prepared from the acetate.

Alternate methods: a) A conc. solution of $HgCl_2$ (20 ml.) is poured into 12 ml. of aqueous ammonia (1:2). The resultant precipitate is treated with a somewhat larger quantity of conc. $Na_2S_2O_3$ solution than is necessary for complete solution. The mixture is heated in a dish and evaporated until pasty; the paste is filtered and washed with hot H_2O.

b) A dry method for the preparation of cinnabar consists in subliming black HgS, grinding the sublimate under H_2O, freeing it from excess sulfur by boiling with a solution of K_2CO_3, washing and drying at 70°C.

SYNONYMS:

Cinnabar, vermilion, Chinese red, cinnabarite.

PROPERTIES:

Black modification: Velvety black amorphous powder (tetrahedral crystals). Soluble in aqua regia and in conc. solutions of alkali sulfides, forming thio salts. Unstable. d (x-ray) 7.69. The mineral metacinnabarite crystallizes as type B3 (zincblende).

Red modification: Scarlet powder, darkens in air. Soluble in aqua regia, less readily soluble than the unstable modification in alkali sulfide solutions. Sublimes at 580°C; d 8.09. Hardness 2-2.5. Hexagonal, deformed NaCl lattice, type B9 (cinnabarite type).

REFERENCES:

L. C. Newell, R. N. Maxson and M. H. Filson in: H. S. Booth, Inorg. Syntheses, Vol. I, New York-London, 1939, p. 19; O. Hausamann. Ber. dtsch. chem. Ges. 7, 1747 (1874).

Mercury (II) Selenide

HgSe

I. $$\underset{271.5}{HgCl_2} + \underset{81.0}{H_2Se} = \underset{279.6}{HgSe} + \underset{72.9}{2\,HCl}$$

A dilute solution of $HgCl_2$ is added in drops (stirring) to a saturated aqueous solution of H_2Se, so that $HgCl_2$ is never present in excess. Air is carefully excluded. If a conc. solution of $HgCl_2$ is used, the precipitate formed consists of yellow $HgCl_2 \cdot 2\,HgSe$.

II. $$\underset{271.5}{HgCl_2} + \underset{98.0}{2\,NaCN} + \underset{280.4}{8\,NH_4OH} + \underset{101.0}{SeO_2} + \underset{192.2}{3\,SO_2}$$

$$= \underset{279.6}{HgSe} + \underset{116.9}{2\,NaCl} + \underset{88.1}{2\,NH_4CN} + \underset{396.4}{3\,(NH_4)_2SO_4} + \underset{72.1}{4\,H_2O}$$

Mercury (II) chloride is added to an equivalent amount of NaCN solution; the mixture is made strongly alkaline with conc. ammonia and an equivalent amount of SeO_2 is added. The mixture is filtered and SO_2 is introduced. The liquid must be maintained alkaline to prevent precipitation of red selenium. The end of the neutralization may be spotted by the reduced rate of absorption of SO_2. The black HgSe is suction-filtered, washed with a dilute ammoniacal NaCN solution followed by H_2O, and dried in a desiccator over P_2O_5.

III. $$\underset{200.6}{Hg} + \underset{79.0}{Se} = \underset{279.6}{HgSe}$$

Stoichiometric quantities of Hg and Se are heated to 550–600°C in a sealed bomb.

The product may be purified by sublimation at 600–650°C in a stream of very pure N_2.

SYNONYM:

Mercuric selenide.

PROPERTIES:

Gray-black (the sublimed material is violet-black) regular crystals with a metallic luster. Sublimes without decomposition

at about 600°C in N_2, CO_2 or vacuum. Soluble in NH_4HSe, giving a red solution. d 8.266. Hardness (of tiemannite) 2.5. Crystal structure: type B3 (zincblende type).

REFERENCES:

I. L. Moser and K. Atynski. Monatsh. Chem. 45, 235 (1925).
II. H. Hahn and G. Störger. Unpublished data.
III. G. Pellini and R. Sacerdoti. Gazz. Chim. Ital. 40, II, 42 (1910); Chem. Zentralbl. 1910, II, 1741.

Mercury (II) Amide Chloride

$HgNH_2Cl$

$$HgCl_2 + 2NH_3 = HgNH_2Cl + NH_4Cl$$
$$271.5 \quad 34.1 \quad 252.1 \quad 53.5$$

A solution of 20 g. of $HgCl_2$ in 400 ml. of H_2O is mixed with 31 ml. of 6N (10%) ammonia. The resultant precipitate is allowed to settle and is then suction-filtered and washed with 180 ml. of cold water. This amount of wash water must be adhered to precisely, since it affects the composition of the product: with larger quantities of H_2O the product assumes a yellow color due to partial formation of $NHg_2Cl \cdot H_2O$. The product is dried at 30°C (exclusion of light); when it appears to be dry, it is ground and dried further at 30°C. Yield 18.5 g.

SYNONYMS:

White mercuric precipitate (infusible); ammoniated mercuric chloride.

PROPERTIES:

White, light-sensitive powder. Insoluble in H_2O; decomposes in H_2O and alcohol. Completely soluble in CH_3COOH. Does not melt on heating, but volatilizes with decomposition. d 5.38.

REFERENCES:

E. Mannerheim. Pharmazeutische Chemie [Pharmaceutical Chemistry], IV, Exercise Compounds, Collection, 682, p. 63 (1921); J. Sen. Z. anorg. allg. Chem. 33, 197 (1903).

Diamminemercury (II) Dichloride

$HgCl_2 \cdot 2NH_3$

L

$$HgCl_2 + 2NH_3 = HgCl_2 \cdot 2NH_3$$
$$271.5 \quad 34.1 \quad 305.6$$

A solution of 5 g. of $HgCl_2$ and 3 g. of NH_4Cl in 100 ml. of H_2O is allowed to react with 20 ml. of 4.5N (8%) ammonia. The

mixture is left to stand six days (frequent shaking). The resultant precipitate consists of small, colorless crystals. It is washed with alcohol and dried in the dark over KOH.

II. In the absence of moisture, the product of theoretical composition is formed in 1.5 days via addition of NH_3 to $HgCl_2$ at room temperature in a vapor pressure eudiometer (cf. Part I, p. 102). The other known ammines are $HgCl_2 \cdot 8\,NH_3$ and $HgCl_2 \cdot 9.5\,NH_3$.

SYNONYM:

White mercuric precipitate (fusible).

PROPERTIES:

Fine rhombic dodecahedra comprise the crystalline, air-stable, white powder. Melting range 247 to 253°C under NH_3 at atmospheric pressure. Soluble in CH_3COOH. Stable as a precipitate in a solution containing more than 1.7 g. of NH_4Cl/100 ml. of H_2O. Melts with decomposition on heating. d 3.77. Crystal structure: cubic with random distribution of Hg.

REFERENCES:

I. D. Strömholm. Z. anorg. allg. Chem. 57, 86 (1908).
II. W. Biltz and C. Mau. Ibid. 148, 170 (1925).

DropBooks

Mercury (II) Iminobromide

$Hg_2(NH)Br_2$

$$\underset{720.8}{2\,HgBr_2} + \underset{51.1}{3\,NH_3} = \underset{576.1}{Hg_2(NH)Br_2} + \underset{195.8}{2\,NH_4Br}$$

I. A solution of 2.16 g. of $HgBr_2$ in 80 ml. of boiling water is mixed with a solution of 0.2 g. of NH_4Br in 100 ml. of 0.1N ammonia. A yellow precipitate forms immediately; it is suction-filtered while still hot, washed with 250 ml. of cold water, and dried over NaOH. Yield 1.4 g. (81%).

II. A concentrated solution of 1.44 g. of $HgBr_2$ and 0.9 g. of NH_4Br (total volume about 30 ml.) is added to 2.6 g. of freshly precipitated HgO. The mixture is shaken for about six hours; it clarifies after 2.5 hours. The precipitate is worked up as in method I.

SYNONYM:

Mercuric iminobromide.

PROPERTIES:

Yellow, light-sensitive powder. Soluble in KCN and KI solutions, insoluble in organic solvents. Shaking with cold, aqueous ammonia yields the bromide of Millon's base (see below).

REFERENCES:

I. W. Rüdorff and K. Brodersen. Z. anorg. allg. Chem. 270, 145 (1952).
II. A. Meuwsen and G. Weiss. Ibid. 289, 5 (1957).

Millon's Base

$$NHg_2OH \cdot x\,H_2O \ (x = 1 \text{ or } 2)$$

$$\underset{433.2}{2\,HgO} + \underset{35.1}{NH_4OH} = \underset{468.3}{NHg_2OH \cdot 2\,H_2O} \xrightarrow{110^\circ C} \underset{450.2}{NHg_2OH \cdot H_2O}$$

Freshly precipitated HgO (see below) is taken up in carbonate-free, approximately 12N ammonia, and shaken in the dark for 14 days. The resultant light-yellow microcrystalline precipitate is filtered and washed with some water. It is dried over silica gel in a desiccator.

This dihydrate of Millon's base may be converted to the brown monohydrate by brief drying (10 minutes at 110°C). This compound is stable in vacuum over silica gel.

The starting HgO is precipitated at 70°C by addition of a solution of 7.5 g. of NaOH in 20 ml. of H_2O to a solution containing 25 g. of $HgCl_2$ in 200 ml. of H_2O.

The starting ammonia solution is prepared by passing 51 g. of CO_2-free NH_3 through 250 ml. of boiled distilled water.

PROPERTIES:

a) Dihydrate: Very fine, yellow, hexagonal crystals, light-sensitive, insoluble in alcohol and ether. Converted to the monohydrate above 110°C. d (x-ray) 7.33. Crystal structure: hexagonal.

b) Monohydrate: Brown, light-sensitive powder. In moist air, the color changes to yellow, with formation of the dihydrate. d (x-ray) 7.05. Crystal structure: hexagonal.

REFERENCE:

W. Rüdorff and K. Brodersen. Z. anorg. allg. Chem. 274, 338 (1953).

Bromide of Millon's Base

NHg_2Br

$$2\,HgBr_2 + 4\,NH_3 = NHg_2Br + 3\,NH_4Br$$
$$720.9 \quad 68.1 \quad 495.1 \quad 293.9$$

Ammonia (5 ml., 24%) is diluted with 400 ml. of water. A solution of $HgBr_2$ in 200 ml. of water, saturated at 20°C, is added with stirring. The resultant yellow precipitate is filtered and washed with water until the filtrate is free of bromide ion. The light yellow product is dried at 110°C and stored in vacuum over silica gel.

The iodide and the nitrate of Millon's base are also readily prepared (see reference below).

PROPERTIES:

Light yellow, finely grained powder. d (pycn.) 7.64, d (x-ray) 7.66. Crystal structure: hexagonal (space group D^4_{6h}).

REFERENCE:

W. Rüdorff and K. Brodersen. Z. anorg. allg. Chem. 274, 338 (1953).

DropBooks

Mercury (I) Thionitrosylate

$[Hg_2(NS)_2]_x$

$$2\,Hg_2(NO_3)_2 + S_4(NH)_4 = 2\,Hg_2(NS)_2 + 4\,HNO_3$$
$$(2\,H_2O) \quad 1122.6 \quad 188.3 \quad 886.7 \quad 252.1$$

A solution of 2.3 g. of $Hg_2(NO_3)_2$ (carefully predried over P_2O_5) in about 60 ml. of dimethylformamide is prepared. Any basic nitrate which may precipitate is filtered off. The solution is cooled in a −70°C bath and 400 mg. of $S_4(NH)_4$, dissolved in a few milliliters of dimethylformamide, is added. The resultant yellow solution is slowly brought to room temperature. A yellow precipitate begins to separate at about 0°C. The mixture is allowed to stand 10 minutes and is filtered on a coarse fritted glass filter. The precipitate is washed with dimethylformamide, followed by acetone. The product is dried in high vacuum, first at room temperature, then for a short time at 100°C. Yield 1–1.5 g.

SYNONYM:

Mercurous thionitrosylate.

PROPERTIES:

Solid yellow substance. Insoluble in all common solvents. Stable at room temperature; detonates when held in a flame. Hydrolyzed by bases, evolving NH_3; reacts with strong acids, forming basic Hg salts, SO_2 and ammonium salts.

REFERENCE:

M. Goehring and G. Zirker. Z. anorg. allg. Chem. 285, 70 (1956).

Mercury (II) Thionitrosylate

$[Hg(NS)_2]_x$

$$\underset{637.4}{2\,Hg(CH_3COO)_2} + \underset{188.3}{S_4(NH)_4} = \underset{585.5}{2\,Hg(NS)_2} + \underset{240.2}{4\,CH_3COOH}$$

A solution of 27 g. of $Hg(CH_3COO)_2$ in absolutely dry pyridine is prepared. Then 1 g. of $S_4(NH)_4$ in 20 ml. of pyridine is added, resulting in the appearance of a blood-red color, followed soon by separation of a fine-grained yellow precipitate. The mixture is mechanically shaken until the supernatant becomes pure yellow: this requires about two hours. During this operation, the temperature should be maintained at 20–25 °C; the reaction is inhibited at lower temperatures. After the shaking, the deposit is washed several times with pyridine (total 80 ml.) and the solvent is decanted. The remaining pyridine is removed by ether extraction. The product is vacuum-dried over conc. H_2SO_4. Yield 2 g. (65%).

PROPERTIES:

Finely divided yellow powder. Insoluble in all common solvents. In water, decomposes with blackening. Stable at room temperature, decomposes at about 140 °C.

SYNONYM:

Mercuric thionitrosylate.

REFERENCE:

A. Meuwsen and M. Lösch. Z. anorg. allg. Chem. 271, 217 (1953).

Diethylmercury

$Hg(C_2H_5)_2$

$$\underset{266.6}{2\,C_2H_5MgBr} + \underset{271.5}{HgCl_2} = \underset{258.7}{(C_2H_5)_2Hg} + \underset{184.2}{MgBr_2} + \underset{95.2}{MgCl_2}$$

Magnesium turnings (25 g.) are covered with 500 ml. of dry ether in a two-liter three-neck flask provided with a dropping

funnel and reflux condenser. Ethyl bromide (125 g.) is gradually added in drops from a funnel. The rate of the reaction, which starts after a few minutes, is regulated by the rate of addition. It may be slowed by cooling with water. When the reaction ceases, the solution is boiled for about 30 minutes, cooled and filtered through glass wool.

The ethereal C_2H_5MgBr solution is treated portionwise (stirring) with 97 g. of $HgCl_2$ in a second three-neck two-liter flask, equipped with a stirrer and a reflux condenser. The addition is spread out over 45 minutes to avoid a too violent reaction. The solution is then boiled for about 10 hours, after which 250 ml. of water is slowly added through the condenser to hydrolyze the excess C_2H_5-MgBr. The ether layer is separated and dried over $CaCl_2$. After removal of the ether by distillation, the residue is distilled under reduced pressure. The $Hg(C_2H_5)_2$ goes over between 97 and 99°C at 100 mm. Yield 55 g. (~60%).

Dimethylmercury may be obtained in a similar manner according to

$$2\,CH_3MgBr + HgCl_2 = Hg(CH_3)_2 + MgBr_2 + MgCl_2.$$

Storage ampoules are first filled with N_2 or CO_2 to avoid explosions during melt-sealing. To avoid the unpleasant results of shattering of the ampoules on explosion (flying glass, etc.), the ampoules should be stored in cotton wool inside well-stoppered powder jars.

DropBooks

PROPERTIES:

Almost odorless, heavy liquid. B.p. (760 mm.) 159°C. Stable to H_2O and air. Gradually decomposes when stored in light (Hg drops appear). Almost insoluble in H_2O, sparingly soluble in alcohol, soluble in ether. d (20°C) 2.466. Very toxic.

The danger of poisoning is especially great when the compound is spilled on a porous surface, such as a laboratory bench or wooden floor. The material is inactivated by hot hydrochloric acid or hot mercuric chloride solution (formation of C_2H_5HgCl).

REFERENCES:

C. S. Marvel and V. L. Gould. J. Amer. Chem. Soc. 44, 153 (1922); E. Krause and A. von Grosse. Chemie der metallorgan. Verbindungen [Chemistry of Oranometallic Compounds], Berlin, 1937.

Mercury (I) Acetate

$Hg_2(CH_3COO)_2$

$$Hg_2(NO_3)_2 + 2\,CH_3COONa = Hg_2(CH_3COO)_2 + 2\,NaNO_3$$

$(2\,H_2O)$			
561.3	164.1	519.3	170.0

A solution of 20 g. of $Hg_2(NO_3)_2$ in 120 ml. of water plus 3.5 ml. of 25% HNO_3 is treated with a solution of 15 g. of sodium acetate in 50 ml. of H_2O. The resultant precipitate is washed with cold water and dried in a desiccator over $CaCl_2$. Yield 13 g.

SYNONYM:

Mercurous acetate.

PROPERTIES:

White, light-sensitive crystal flakes (tinged with gray). Solubility (15°C) 0.75 g./100 ml. H_2O. On boiling and in light the compound in solution disproportionates to Hg and Hg (II) acetate; the mercuric salt then hydrolyzes to a yellow, insoluble basic salt. Readily soluble in dilute acetic acid, insoluble in alcohol and ether. Decomposes on heating, forming a residue of black flakes.

REFERENCE:

Ullmann. Enzykopädie d. techn. Chemie [Encyclopedia of Ind. Chemistry], 2nd ed., IV, 679.

Mercury (II) Acetate

$Hg(CH_3COO)_2$

$$HgO + 2\,CH_3COOH = Hg(CH_3COO)_2 + H_2O$$

216.6	120.1	318.7	18.0

A solution of 20 g. of yellow HgO in 30 ml. of 50% CH_3COOH is prepared on a water bath. It is filtered through a jacketed filter heated with hot water, and the filtrate is cooled with ice. The crystals are suction-dried and washed with ethyl acetate. The product is recrystallized from hot ethyl acetate or from hot water slightly acidified with acetic acid. The salt is dried in a vacuum desiccator over $CaCl_2$.

Use: As a mercurizing and oxidizing agent and for the absorption of ethylene.

SYNONYM:

Mercuric acetate.

PROPERTIES:

Nacreous, light-sensitive crystalline flakes. On storage acquires a yellow tinge and an odor of CH_3COOH (formation of a basic salt). M.p. 178–180°C, decomposes at higher temperatures. Solubility (0°C) 25 g., (19°C) 36.4 g./100 ml. H_2O (and about 100 g. at 100°C with partial dec.). The compound in 0.2N aqueous solution is approximately 30% hydrolyzed; the yellow basic salt precipitates on diluting or heating; Soluble in ethyl acetate. d^{23} 3.286.

REFERENCE:

Gmelin-Kraut. Hdb. anorg. Chem. [Handbook of Inorg. Chem.], 7th ed., V2, 826, Heidelberg, 1914, modified.

Mercury (II) Cyanide

$Hg(CN)_2$

I. $$\underset{218.6}{HgO} + \underset{54.1}{2\,HCN} = \underset{252.7}{Hg(CN)_2} + \underset{18.0}{H_2O}$$

The crystalline material is obtained by evaporation of a solution of HgO in aqueous HCN. The product is recrystallized, dried at 50°C, ground and redried.

II. $$\underset{1/18\ 195.0}{9\,HgO} + \underset{85.9}{Fe_4[Fe(CN)_6]_3} + \underset{16.2}{9\,H_2O} =$$

$$\underset{227.4}{9\,Hg(CN)_2} + \underset{42.8}{4\,Fe(OH)_3} + \underset{27.0}{3\,Fe(OH)_2}$$

One part of HgO is digested for a few hours on a water bath with one part of Prussian blue and 10 parts of H_2O. The crystals separate on evaporation of the solution.

SYNONYM:

Mercuric cyanide.

PROPERTIES:

Colorless, prismatic, tetragonal crystals. Decomposes into Hg and $(CN)_2$ at 320°C. Solubility (0°C) 8 g., (100°C) 53.9 g./100 ml.

H_2O; (19.5°C) 10.1 g./100 g. ethanol; (19.5°C) 44.1 g./100 g. methanol. d 3.996. Crystal structure: type Fl_1 [$Hg(CN)_2$ type].

REFERENCES:

I. W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).
II. Gmelin-Kraut. Hdb. anorg. Chem. [Handbook of Inorg. Chem.], 7th ed. V2, 832, Heidelberg, 1914.

Potassium Tetracyanomercurate (II)

$K_2Hg(CN)_4$

$$\underset{252.7}{Hg(CN)_2} + 2\,\underset{130.2}{KCN} = \underset{382.9}{K_2Hg(CN)_4}$$

I. A solution of stoichiometric quantities of $Hg(CN)_2$ and KCN is evaporated to induce crystallization. The product is recrystallized and dried at 80°C.

II. Treatment of a suspension of $Hg(CN)_2$ in liquid HCN with the stoichiometric quantity of KCN produces $KHg(CN)_3$, in addition to $K_2Hg(CN)_4$.

SYNONYM:

Potassium mercuricyanide.

PROPERTIES:

Colorless, octahedral crystals. Solubility (20°C) 1 g./35 g. of 80% v./v. alcohol. d 2.420. Crystal structure: type $H1_1$ (spinel type).

REFERENCES:

I. W. Biltz. Z. anorg. allg. Chem. 170, 161 (1928).
II. G. Jander and B. Grüttner. Ber dtsch. chem. Ges. 81, 118 (1948).

Mercury (I) Thiocyanate

$Hg_2(SCN)_2$

$$\underset{(2\,H_2O)\ 561.3}{Hg_2(NO_3)_2} + 2\,\underset{194.3}{KSCN} = \underset{517.4}{Hg_2(SCN)_2} + 2\,\underset{202.2}{KNO_3}$$

A slightly acid solution of $Hg_2(NO_3)_2$, freed of mercuric ions by means of metallic Hg, is treated with somewhat less than the

stoichiometric amount (~75%) of KSCN solution. A dark-gray salt precipitates at first; after standing for several days (repeated stirring), it becomes completely white. It is washed several times with boiling H_2O.

SYNONYMS:

Mercurous thiocyanate; mercury (I) rhodanide.

PROPERTIES:

Colorless, light-sensitive powder. Insoluble in H_2O, soluble in KSCN solution, precipitating Hg. Decomposes on heating, forming a foamy mass. d 5.318.

REFERENCE:

K. Huttner and S. Knappe. Z. anorg. allg. Chem. 190, 27 (1930).

Mercury (II) Thiocyanate

$$Hg(SCN)_2$$

$$\underset{(H_2O)}{Hg(NO_3)_2} + 2\,KSCN = Hg(SCN)_2 + 2\,KNO_3$$

342.6 194.3 316.8 202.2

DropBooks

A $Hg(NO_3)_2$ solution, acidified with a few drops of HNO_3, is treated with the stoichiometric amount of KSCN solution. The resultant crystalline precipitate is suction-filtered and washed with H_2O. The product may be recrystallized from hot H_2O or alcohol. Yield 80%.

SYNONYMS:

Mercuric thiocyanate, mercuric sulfocyanate.

PROPERTIES:

Colorless, fibrous needles or nacreous flakes. Solubility (25°C) 0.069 g./100 ml. H_2O. The solubility in alcohol and boiling H_2O and in KSCN solution is higher, in ether lower. Decomposes with swelling on heating to 165°C.

REFERENCE:

W. Peters. Z. anorg. allg. Chem. 77, 157 (1912).

Potassium Tetrathiocyanomercurate (II)

$K_2Hg(SCN)_4$

$$Hg(SCN)_2 + 2\,KSCN = K_2Hg(SCN)_4$$
$$316.8 \qquad 194.3 \qquad 511.1$$

A boiling solution of 20 g. of KSCN in 100 ml. of H_2O is mixed with 31.7 g. of $Hg(SCN)_2$. The HgS precipitating on cooling is filtered off. The filtrate is concentrated on a water bath until crystallization. The solution then solidifies on further cooling to a white, fibrous crystalline mass. It is suction-filtered and dried over P_2O_5.

SYNONYM:

Potassium mercurithiocyanate.

PROPERTIES:

Brilliant white crystal needles. Readily soluble in cold water, soluble in alcohol, insoluble in absolute ether.

REFERENCE:

A. Rosenheim and R. Cohn. Z. anorg. allg. Chem. 27, 285 (1901).

SECTION 21

*Scandium, Yttrium, Rare Earths**

K. WETZEL

Pure Scandium Compounds

Scandium may be freed of accompanying elements by extraction of its thiocyanate with ether.

A) PURIFICATION OF SMALL QUANTITIES

One gram of the oxide (which should contain as little Ti, Zr and Hf as possible) is dissolved in dilute hydrochloric acid. The solution is evaporated on a water bath until a moist crystal paste is obtained (see note, p. 1126). This is taken up in 60 ml. of 0.5N *HCl*. Then 53 g. of NH_4SCN is added (the final volume should be about 100 ml.) and the mixture is shaken with 100 ml. of ether. If a separatory funnel is used, complete phase separation is often difficult to achieve since the stopcock may become plugged with solid decomposition products of HSCN during the removal of the bottom phase. It is therefore advisable to use a flask such as that in Fig. 284, which has a ground glass stopper at the top, and to use a vacuum in order to transfer the top (or ether) phase into flask *c* via tube *b*. Dilute HCl (5–10 ml.) is added to the separated top phase, the ether is evaporated, and the dry residue is treated on a water bath with conc. nitric acid, added in drops (caution! violent reaction). The mixture is then boiled with some additional conc. nitric acid until the orange red HSCN decomposition products disappear. The solution

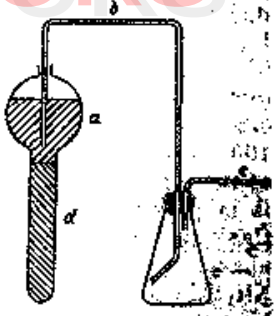

Fig. 284. Ether extraction of scandium thiocyanate: *a* ether solution, *b* siphon, *c* storage flask, *d* aqueous solution, *e* vacuum connection.

*In the following text, the rare earths are designated by the general symbol Ln.

is diluted with water and pure scandium is precipitated with dilute ammonia.

This procedure almost completely removes Mg, Ca, Y, the lanthanides, Th and Mn; it also frees the scandium, to a large extent, of Ti, Zr, Hf, U and Fe. However, the product is still contaminated with varying amounts of Be, Al, In, Mo, Re, Fe and Co.

NOTE:

Very impure raw material samples often yield a noncrystallizing sirup on evaporation of the HCl solution; this sirup should not be heated too long because there is a danger of extensive hydrolysis. A small excess of HCl does not interfere at this stage.

B) PURIFICATION OF LARGE QUANTITIES

The crude oxide (60 g.) is dissolved in hydrochloric acid and evaporated carefully on a water bath until a moist crystalline mass is formed.

(If the mass should become sirupy instead of crystalline, the evaporation is discontinued and the mixture is diluted in 400–500 ml. of water. Then dilute ammonia is carefully added until the yellow end-point of tropeolin 00, 30 ml. of 2N HCl is added, and the volume is made up to 600 ml. with water. The purification procedure is then continued as described below.)

The paste is dissolved in 600 ml. of 0.1N HCl. If Ti or considerable quantities of Zr and Hf are initially present, hydrolysis products of these elements may still remain; they are filtered off before the next step. The solution is then allowed to react with 500–550 g. of NH_4SCN and shaken with one liter of ether in a three-liter flask (not a separatory funnel). Just as in method (A), as much of the ether layer as possible is transferred to a second flask containing 100 ml. of a saturated aqueous solution of NH_4SCN. The acid content of the ether layer, which reaches 0.06N (in HSCN) in the first flask, is largely neutralized by slow addition of 27 ml. of 2N ammonia (the flask is vigorously shaken during this addition). The ether is then shaken in a third and fourth flask each time with 100 ml. of 45% NH_4SCN solution. The Sc is obtained from this purified ether phase by extraction, in a separatory funnel, with pure water (portions of 250–500 ml.). The extraction is continued until the aqueous layer ceases to yield a precipitate on addition of dilute ammonia (any iron in the starting material will concentration in the first 250–500 ml. of aqueous extract). About 2–3 liters of water is necessary to extract 40–50 g. of Sc_2O_3 from one liter of ether. The aqueous phase remaining in the first flask is now acidified with 30 ml. of 2N HCl and the operation with one liter of ether is repeated (reuse the aqueous solutions in flasks 2 to 4.) A second repetition of the extraction procedure yields the last traces of Sc.

Such a purification of an oxide initially containing 75–80% Sc_2O_3, 8–9% ZrO_2, 0.8–0.9% HfO_2, 1–2% Y_2O_3, 0.5% Dy_2O_3, 1% Er_2O_3, 0.5% Tm_2O_3, 6–8% Yb_2O_3, and 1% Lu_2O_3 gave a 90% yield of Sc_2O_3. Spectroscopic analysis (x-ray) revealed no other rare earth impurities nor Zr and Hf in this product (limit of detection: 0.1%); the remaining 10% of the scandium oxide present in the raw material was also obtained in greatly concentrated form. After conversion to the oxide, the residue left in the first flask contained less than 0.5% Sc_2O_3.

Alternate methods: a) Fractional condensation of the chlorides.

b) Fractional sublimation of the acetylacetonates.

c) According to Vickery, pure Sc compounds may be obtained by ion exchange.

REFERENCES:

W. Fischer and R. Brock. Z. anorg. allg. Chem. 249, 168 (1942); this paper also reexamines several other procedures for extraction of scandium; R. C. Vickery, J. Chem. Soc. (London) 1955, 245.

DropBooks

Treatment of Monazite Sand

Monazite is the orthophosphate of the cerium group of rare earths; it contains oxides of the cerium group (50–70%), oxides of the Y group (1–4%) ThO_2 (1–20%), varying quantities of $ThSiO_4$, and small amounts of SiO_2, Fe_2O_3 and Al_2O_3.

A) EXTRACTION WITH SULFURIC ACID

The monazite sand is ground in a ball mill (final product approx. U.S. 30 mesh). Conc. H_2SO_4 (3.25 kg.) is heated to 200°C in a six-liter porcelain dish, and 3.5 kg. of ground sand is gradually added in small portions (efficient stirring is necessary). Heating and stirring are continued for 30 minutes after completion of the addition, until a dark gray, quite firm paste is obtained.

The paste is slowly poured (stirring) into 25 liters of cold water, and stirring is continued for one hour. If the solution is still warm after this time, ice is added until the temperature drops below 25°C, since the rare earth sulfates are more soluble in cold than hot water. The residue is allowed to settle, the clear supernatant is decanted, and the solid is suction-filtered and washed several times with cold water. The residue consists of SiO_2, TiO_2, ZrO_2 and unreacted monazite. The residues of several extractions may be combined and subjected to a second H_2SO_4 treatment.

B) PRECIPITATION OF Th IN THE FORM OF ThP_2O_7

The filtrate, which contains H_2SO_4, H_3PO_4, Th and the rare earths, is diluted to 168 liters and stirred for one hour in an earthenware or wooden vessel. The nascent, slightly blue-gray, heavy, gelatinous precipitate is allowed to settle for 8–12 hours. It consists of ThP_2O_7 contaminated with phosphates of cerium and of other rare earths. The precipitation is complete when no additional solid separates on further dilution. The ThP_2O_7 is filtered off and washed with water.

C) PRECIPITATION OF THE RARE EARTHS IN THE FORM OF $Na_2SO_4 \cdot Ln_2(SO_4)_3 \cdot 2H_2O$ OR $Ln_2(C_2O_4)_3 \cdot 5H_2O$

The rare earths are isolated from the filtrate by agitation in the presence of finely ground Na_2SO_4 until the absorption bands of Nd are no longer observable through a 5-cm. layer of the clear supernatant. The precipitate is filtered off, washed and dried at 110°C [if the starting material contains large amounts of yttria earths (i.e., xenotime, YPO_4) it is best to precipitate with solid oxalic acid, since the double sodium yttria sulfates have appreciable solubilities in water].

A first crude separation of the ceria earths from the yttria earths is achieved by adding solid oxalic acid to the filtrate from the double sulfate precipitation. Use of a saturated solution of oxalic acid yields a precipitate which is difficult to filter and necessitates further dilution of the solution.

D) CONVERSION OF THE SULFATES OR OXALATES TO THE OXIDES

The double sulfates or oxalates are mixed with water and stirred to a thick paste, which is allowed to react with slightly more than the stoichiometric quantity of solid NaOH, which is added in small portions with constant stirring at high heat. As the reaction proceeds, the paste becomes increasingly liquid and stirring is easier. The reaction is brought to completion by further heating and stirring for one hour. The hydroxides are transferred to a 30- to 40-liter earthenware container and stirred with 20–30 liters of water. The precipitate is allowed to settle, the supernatant is siphoned off, and the washing is repeated until the liquid gives only a weak alkaline reaction. The hydroxides are dissolved in conc. nitric acid (add 3% H_2O_2 if large amounts of Ce are present). This nitrate solution serves as starting material for further workup.

Further separation of the resultant mixture of rare earths and isolation of individual components are described in later procedures in this section; in particular, see the preparation of pure La, Pr

and Nd compounds from ceria earths by ion exchange and the preparation of pure Ce, Sm, Eu and Yb compounds.

REFERENCES:

D. W. Pearce, R. A. Hanson, J. C. Butler, W. C. Johnson and W. O. Haas in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 38; S. J. Levy. The Rare Earths, London, 1924, pp. 18, 71, 79.

Treatment of Gadolinite

Gadolinite is an yttria earth-beryllium-iron (II) silicate; its approximate composition is $Y_2Be_2FeSi_2O_{10}$, and it contains up to 50% rare earth oxides and about 10% BeO.

A) EXTRACTION, SEPARATION OF SILICIC ACID

The gadolinite is pulverized in a ball mill to a size passing through a U.S. 140-mesh sieve. Two kilograms of this material are mixed with seven liters of conc. HCl and evaporated (stirring) in a shallow porcelain dish placed on a sand bath; the evaporation is continued until a stiff paste is obtained (1.5 days required). The residue while still hot is taken up in 2-3 liters of hot water, suction-filtered and pressed dry.

To complete the extraction, the residue is again treated as above with 0.5 liter of conc. hydrochloric acid, taken up in one liter of water, suction-filtered, and washed with 0.5 liter of hot, dilute hydrochloric acid. The residue (SiO_2 and impurities not attached by hydrochloric acid) is discarded; it contains only about 0.5% of the rare earths present in the starting material.

B) PRECIPITATION WITH OXALIC ACID

The combined filtrates from (A) are diluted with water to twice their volume and heated to 60°C; a thin stream of a hot solution of 1400-1500 g. of oxalic acid dihydrate in two liters of water is then added with stirring. The mixture is kept warm overnight in a covered container; the precipitate is suction-filtered while still warm and washed with warm water. This yields about 95% of the rare earths initially present. Large quantities of rare earth oxalates are best converted to other compounds by calcining in a stream of air at 600-700°C. The material is spread in a thin layer in a large crucible furnace and heated until the transient gray color disappears again. The oxides can then be readily dissolved in acids. They contain no more than about 0.1% Fe_2O_3 and 0.15% SiO_2.

PropBooks

C) PRECIPITATION WITH NH_3

The iron concentrates in the filtrate of the oxalate precipitation so that it constitutes more than 50% of the total metals present. To separate the Be and the rare earths, the latter are precipitated with NH_3 as the hydroxides (after transient reduction of the iron to the divalent state). The filtrate of operation (B) (two liters) is diluted with six liters of water in a 10-liter flask. The flask is provided with a dropping funnel, as well as gas inlet and outlet tubes; the gas inlet tube reaches to the bottom of the flask and the outlet terminates at the neck. The solution is heated to 60°C and the necessary amount of $KMnO_4$ [determined by testing a very dilute sample of the solution with Mn (II)] is added with efficient mixing to oxidize the oxalic acid. The highest possible concentration of $KMnO_4$ should be used. Then 500–700 g. of solid NH_4Cl is added and the mixture is brought to a boil while SO_2 is passed through. The solution is maintained at the boiling point for an additional 30 minutes, a slow stream of SO_2 being bubbled through all the time. The flame is then removed, the SO_2 is replaced by a stream of H_2, and conc. carbonate-free ammonia is added until no further precipitation occurs. The precipitate should be pure white. A brownish color indicates incomplete reduction of the Fe; a greenish tinge [impure $Fe(OH)_2$] indicates that the amount of NH_4Cl added was insufficient. In either case, the addition of ammonia is discontinued, the precipitate already formed is redissolved in hydrochloric acid, and the procedural fault is corrected. If the precipitate assumes a greenish color only toward the end of the operation, this is an indication that $Fe(OH)_2$ has begun to deposit because an excess of NH_3 is present in solution.

After completion of the precipitation the mixture is allowed to cool to 45°C, and a freshly prepared solution of 70 g. of $Na_2S_2O_4$ in 500 ml. of water and 20 ml. of dilute ammonia is added with efficient mixing. The passage of H_2 is discontinued and the precipitate is suction-filtered and washed with a warm (maximum 45°C) solution of 10 g. of $Na_2S_2O_4$ and 20 g. of NH_4Cl in one liter of water, followed by one liter of pure water. The filtrate and wash water are discarded. The rare earths which have remained in solution after the oxalate precipitation, as well as the Be, are thus quantitatively precipitated. A solution in which the weight ratio $BeO:Ln_2O_3:Fe_2O_3 \approx 1:0.2:1.6$ yields a precipitate in which this ratio is 1:0.2:0.05–0.03.

D) SEPARATION AND RECOVERY OF THE Be

The moist hydroxide precipitate is dissolved in the minimum amount of warm glacial acetic acid and evaporated to complete dryness on a sand bath. Basic beryllium acetate $Be_4O(CH_3COO)_6$

is distilled from the residue at atmospheric pressure (m.p. 284°C; b.p. 330°C; cf. the procedure for the preparation of basic beryllium acetate, p. 901). The residue from this Be separation may be purified by another gadolinite extraction.

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W. Fischer. Z. anorg. allg. Chem. 250, 72 (1942).

Pure La, Pr and Nd Compounds from Cerium Earths by Ion Exchange

Rare earth mixtures are efficiently separated by elution of complexes. Among the complexing agents which are usable as eluents, these which act as chelating agents possess significant advantages. A two-column process is usually employed: the first column is charged with the rare earth mixture and the second column with a suitable auxiliary cation. If the chelating agent used is readily soluble in water (for example, ethanolamine diacetic acid) the material in the second (or bottom) column may be in the H form.

The following process is suitable for rapid laboratory-scale separation of cerium earths: the cerium is removed from the mixture by precipitation with $KMnO_4$ and Na_2CO_3 (see below, preparation of pure Ce compounds). The remaining compounds are adsorbed on 250 ml. of a cation exchange resin (Dowex 50 or Wofatit KPS-200; particle size 0.2–0.4 mm.). The resin is then placed in an ion-exchange column (I.D. 4 cm.) which is partly filled with water. A second column of the same I.D. is filled in the same manner with 350 ml. of the resin in the Zn form.

The eluent flows successively through the two columns; it contains 2% of nitrilotriacetic acid and is buffered with NH_3 to a pH of 7.0. If the eluate flow rate is not less than 0.5 ml. per minute, there is no danger of formation of precipitates inside the columns. The eluate is collected in fractions; the lanthanides appear in the order of increasing ionic radius. The La, which remains in the columns after elution of the heavier earths, may itself be rapidly eluted with a solution containing 4% nitrilotriacetic acid and 2.4% NH_4Cl (pH 9).

The eluate fractions are brought to a boil and the rare earths precipitated with oxalic acid. The mixtures are allowed to stand for 20 minutes at 80°C and filtered hot, and the solids are calcined to the oxides. The first fractions, which may contain minute quantities of Zn, are reprecipitated. More than 70% of the nitrilotriacetic acid used in the process can be recovered from the eluate by precipitation with HCl.

Starting from 63 g. of the mixed oxide (14.7% La_2O_3, 23.5% Pr_6O_{11}, 54% Nd_2O_3, 5.4% Sm_2O_3, 2.4% heavier earths), this method gave 8.3 g. of La_2O_3 (yield 90%, purity > 99.5%), 10.3 g. of Pr_6O_{11} (yield 70%, purity > 99%) and 30 g. of Nd_2O_3 (yield 88.5%, purity > 99%) in 50 hours of elution.

The method is also applicable to the yttrium earths, although in this case it requires more preliminary effort and takes longer.

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L. Wolf and J. Massonne. Chem. Techn. 10, 290 (1958); L. Wolf and J. Massonne, J. prakt. Chem. (4) 275, 178 (1956); L. Holleck and L. Hartinger. Angew. Chem. 66, 586 (1954); 68, 411 (1956); F. H. Spedding and J. E. Powell in: F. C. Nachod and J. Schuber, Ion Exchange Technology, New York, 1956, p. 365; J. Loriers and J. Quesney. Comptes Rendus Hebd. Séances Acad. Sci. 239, 1643 (1954); J. Loriers. Ibid. 240, 1537 (1955).

Pure Cerium Compounds

I. PRECIPITATION WITH Na_2CO_3 AND $KMnO_4$

A nitric acid solution of 250 g. of cerium earths, which should consist only of nitrates, is diluted to one liter and brought to a boil, and the pH is adjusted to 2-3 with aqueous Na_2CO_3. This already precipitates some of the cerium in the form of Ce (IV) hydroxide. A solution of $KMnO_4$ is then added until the red color persists, the mixture is reheated to the boiling point, and the cerium is precipitated by adding (with constant stirring) a solution of $KMnO_4$ and Na_2CO_3 (mole ratio 1:4). The pH gradually reaches 4 and the red color becomes more intense; stirring at the boiling point is then continued for an additional 10 minutes and the precipitate is suction-filtered and washed with hot water. The filtrate contains minute amounts of cerium, in addition to the other rare earths. If it is desired to isolate the last traces of Ce, the pH of the boiling filtrate is adjusted to 5-6 with aqueous Na_2CO_3. The resultant precipitate consists of carbonates containing all the Ce present.

The cerium is isolated from the residues [which consist of Ce (IV) and Mn (IV) hydroxides] by solution of the residues in conc. hydrochloric acid and precipitation in the form of the oxalate. The precipitate is calcined to CeO_2 (96% yield, 99.5% pure).

II. PRECIPITATION WITH $CaCO_3$ AND $KBrO_3$

The following procedure is suitable for a raw material mixture containing 40-50% CeO_2: a nitric acid solution containing about 4100 g. of the rare earth oxides (total of 12 liters) is divided in

three equal portions. The solutions are heated in procelain dishes and adjusted to pH 2.7 by adding $CaCO_3$ (mechanical stirring). Then 100 g. of $KBrO_3$ is added and the solutions are concentrated to one liter (see note below). This procedure is repeated several times to achieve complete oxidation and hydrolysis. If bromine vapor escapes during the evaporation, the pH is readjusted to 2.7 by adding further $CaCO_3$. The mixtures are then diluted to five liters, heated almost to the boiling point, and allowed to settle overnight.

The supernatant liquors are decanted, combined and, after addition of 60 g. of $KBrO_3$, evaporated to 2–3 liters. The mixture is then diluted to eight liters, brought to a boil, and again decanted.

The combined precipitates are boiled in six liters of water, the supernatant liquor is decanted, and the precipitate is suction-filtered through a Büchner funnel. The mother liquor is combined with the solution containing the other rare earths.

Other cerium compounds, for example, the basic nitrates, may be purified and converted to the oxides by boiling 50 g. of the moist starting material with 200 ml. of 3N Na_2CO_3 solution. The basic carbonate is filtered off and washed with 50 ml. of water. The product is dissolved in 16 N HNO_3 containing 3% H_2O_2.

This method gives 99.8% pure CeO_2 in 97.6% yield.

NOTE:

The Ce (III) seems to oxidize during the evaporation in the hot conc. solution, while the hydrolysis of the resultant Ce (IV) takes place in the hot dilute solution.

DropBooks

III. ETHER EXTRACTION OF Ce (IV) NITRATE

Very pure CeO_2 may be prepared from the commercial raw material by the following combined procedure: ten parts of crude oxide and seven parts of hydroquinone (reducing agent) are dissolved in boiling conc. hydrochloric acid. The hydroquinone oxidation products are destroyed by oxidative degradation with H_2O_2 in ammoniacal solution, followed by evaporation with conc. nitric acid. Since it is accompanied by foaming, this operation must be carried out in a large vessel. If necessary the cerium may also be freed of organic contaminants by precipitation with oxalic acid, followed by solution of the precipitate in conc. nitric acid.

If the starting material also contains thorium, the oxalate is boiled with a concentrated, neutral to slightly ammoniacal, solution of ammonium oxalate; the precipitate is suction-filtered and thoroughly washed. Repetition of this operation yields a solution of $(NH_4)_4Th(C_2O_4)_4$ which contains all the thorium initially present.

The nitric acid solution of nitrates, which is obtained in either case, is evaporated to dryness; it is then treated with NH_4NO_3

(same weight as the initial CeO_2) and evaporated several times with conc. HNO_3 until orange-red $(NH_4)_2Ce(NO_3)_6$ begins to precipitate from the deep red solution. The precipitate is filtered off on a fritted glass filter (additional double nitrate may be recovered from the filtrate by further evaporation). The product is recrystallized from conc. nitric acid, dissolved in 6N nitric acid (free of nitric oxide), and extracted with peroxide-free ether (nitric oxides and peroxides reduce Ce^{4+}). The residual material in the aqueous solutions should be reoxidized by evaporation with conc. nitric acid and extracted with ether, since the solutions still contain appreciable quantities of Ce^{3+}.

The combined ether extracts are distilled, water being added during distillation. The cerium nitrate may be reprecipitated with water containing a hydrazine salt, which serves as a reducing agent.

The resultant cerium nitrate solution, which is about 2N in HNO_3, is filtered and slowly added in drops to a hot, concentrated solution of oxalic acid. The finely crystalline precipitate of cerium oxalate is suction-filtered, washed with a large quantity of water, dried and calcined to the oxide.

The oxide may also be obtained by evaporation of the nitrate solution, followed by thermal decomposition of the cerium nitrate.

Preparation of cerium compounds of especially high purity (for neutron bombardment): Peppard et al. recommend extraction of the Ce (IV) from a 10M HNO_3 solution with a 0.75M or 0.30M solution of bis(2-ethyl)hexyl orthophosphate in n-heptane [D. F. Peppard, G. W. Mason and S. W. Moline, J. Inorg. Nuclear Chem. 5, 141 (1957)].

PROPERTIES:

Cerium (IV) oxide is white with a slight yellow tinge; the color is a function of particle size. Even slight contamination with Pr or Tb (0.005%) produces a distinct pink color; higher amounts cause a red-brown color. The calcined material is soluble in acids only in the presence of reducing agents. d (x-ray) 7.172. Crystal structure: type C1 (CaF_2 type).

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II. D. W. Pearce, J. C. Butler, W. C. Johnson and W. O. Hass in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 48; R. Bock, Angew. Chem. 62, 375 (1950).

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Pure Samarium Compounds

I. REDUCTION WITH CALCIUM AMALGAM

$$\underset{513.8}{2\,SmCl_3} + \underset{40.1}{Ca(Hg)} = \underset{442.7}{2\,SmCl_2} + \underset{111.0}{CaCl_2}$$

A solution of 180–240 g. of anhydrous rare earth chlorides in 600–700 ml. of absolute ethanol is placed in a thick-wall, rubber-stoppered separatory funnel. After addition of 7–10 g. of Ca in the form of a 1% amalgam (see p. 1804 for preparation), the separatory funnel is stoppered and vigorously shaken. Since this reduction to Sm (II) is accompanied by formation of calcium ethoxide and consequent evolution of H_2, the flask must be frequently vented by opening the stopcock (without, however, allowing air to enter). The initially yellow solution soon becomes dark; after a few minutes the color becomes dark brown-red and precipitation of $SmCl_2$ begins. The Ca becomes exhausted after 20 minutes. The funnel is inverted so that it rests on the rubber stopper, a Bunsen valve is attached to the outlet tube, and the stopcock is opened. After 10 minutes, the CaO present in the mixture is neutralized by adding (through the funnel stem) 2–3 ml. of HCl-saturated anhydrous ethanol, and the funnel is vigorously shaken. The precipitate should turn bright red. After 30 minutes the Hg is separated and the finely crystalline precipitate of $SmCl_2$ is centrifuged in the absence of air. The mother liquor is decanted and the precipitate is freed of the adhering solution by shaking with air-free absolute ethanol, followed by centrifugation.

Further purification is achieved by taking up the precipitate in water, in which it is oxidized to Sm (III) and forms the basic chloride. Dilute hydrochloric acid is added and the mixture is heated on a water bath until the mercury left in the $SmCl_2$ has agglomerated and can be filtered off. The yellow solution is concentrated until crystallization just starts, and then saturated with HCl while cooling in ice. The precipitated hexahydrate is dehydrated and again reduced. The $SmCl_2$ obtained after this last purification procedure contains only a few percent of Eu.

The Eu may be removed by electrolysis of an alkaline acetate solution of the Sm–Eu mixture in the presence of lithium nitrate; a mercury cathode is used. Onstott, starting from a precipitate containing 1.6% Eu_2O_3, was able to obtained a preparation entirely free of Eu in one electrolysis run.

B. REDUCTION WITH Mg + HCl

Another process suitable for the separation of Sm from rare earth mixtures consists in reducing the samarium, in the form of hydrated chlorides in ethanol or ethanol-dioxane, by means of Mg + HCl. A mixture containing 3% Sm can be concentrated to 55% Sm in a simple run.

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Pure Europium Compounds

I. $EuCl_2 \cdot 2H_2O$

A conc. solution (d 1.35, 100 ml.) of rare earth chlorides containing about 70% Eu (balance Nd, Sm and Gd) is placed together with a few milliliters of conc. hydrochloric acid in a one-liter wide-neck flask. Zinc amalgam granules (100 g., U. S. standard mesh 80) are added, and the flask is stoppered and vigorously shaken by hand. From time to time it is held in front of the slit of a spectrometer to observe the absorption bands. The initially almost colorless solution turns yellowish; after about 30-40 minutes the Eu 5253 Å band disappears, indicating complete reduction to Eu (II). The solution is decanted from the remaining Zn while protected by a CO_2 blanket and poured into a second one-liter flask; the flask is closed with a two-hole stopper carrying a 250-ml. dropping funnel and a gas outlet capillary. Crystallization of $EuCl_2 \cdot 2 H_2O$ starts after addition of the first 200 ml. of conc. hydrochloric acid; it reaches a maximum rate after 500 ml. has been added. This procedure precipitates 90% of the Eu present. After 2-3 hours of standing, the well-cooled mixture consists of almost equal volumes of pure white crystals with a faintly blue fluorescence and an essentially colorless mother liquor.

The air-sensitive crystals are filtered under CO_2 through a cotton wool filter and suction-dried as far as possible. If oxidation does occur, the filter cake becomes hot and evolves HCl gas. The Eu may be further purified by redissolving the product chloride under CO_2. The operation should be repeated five times. Finally the product is filtered through a fritted glass filter (under a CO_2 blanket) and washed with 10% methanolic HCl. The alcohol and the HCl can then be removed by slight heating in a fast CO_2 stream.

Another method for removal of traces of other earths present in crude europium consists in reduction of the europium with Zn amalgam in HCl solution. Then the trivalent earths are precipitated with carbonate-free ammonia. The Eu (II) remains in solution.

II. $EuSO_4$

$$\underset{516.7}{2\,EuCl_3} + \underset{65.4}{Zn} = \underset{445.6}{2\,EuCl_2} + \underset{136.3}{ZnCl_2}$$

$$\underset{222.9}{EuCl_2} + \underset{98.1}{H_2SO_4} = \underset{248.1}{EuSO_4} + \underset{72.9}{2\,HCl}$$

A solution of 3.5 g of Eu_2O_3 in 5.4 ml of 6N HCl is diluted to about 200 ml. A Jones reductor (height 40 cm., diameter 2 cm.) is filled with 1% Zn amalgam granules (0.5–1 mm.), which are then washed with 200 ml. of 0.1N HCl. When the wash liquor just covers the zinc, the outlet of the reductor is dipped in 50 ml. of 8M H_2SO_4 in a 600-ml. beaker covered with a round piece of paper. Carbon dioxide is then introduced into the beaker to expel the air. The $EuCl_3$ is passed slowly (2 ml./min.) through the reductor, followed by 150 ml. of 0.1N HCl. Very light, white, hairlike crystals of α-$EuSO_4$ are the first product. This mixture is heated to 80°C in a CO_2 atmosphere, resulting in conversion of the α-form to the stable β-form, which is less soluble in dilute H_2SO_4 and settles as a dense crystalline mass. The mixture is cooled to room temperature, and the white $EuSO_4$ is filtered and washed with dilute hydrochloric acid, followed by a few milliliters of HCl-acidified methanol. The CO_2 blanket is not necessary during the filtration. The product may be dried in air at 75°C. The yield is 90% of 99.7% $EuSO_4$.

PROPERTIES:

White, microcrystalline. Sparingly soluble in water; d (25°C) 4.98. Isomorphous with $SrSO_4$ and $BaSO_4$.

III. $EuCO_3$

$$\underset{248.1}{EuSO_4} + \underset{106.0}{Na_2CO_3} = \underset{212.0}{EuCO_3} + \underset{142.1}{Na_2SO_4}$$

First, 5 g. of $EuSO_4$ is gradually added to 300 ml. of a vigorously boiling, oxygen-free solution which is 1N in Na_2CO_3 and 0.4N in NaOH (12.6 g. of $NaHCO_3$ and 10.8 g. of NaOH). After a short time, the solution turns dark; the color disappears on further boiling, and a dense, lemon yellow, crystalline precipitate of $EuCO_3$ is

formed. This precipitate is filtered and dried in air at 75°C. An almost 100% pure product is obtained in 90% yield.

When larger quantities of $EuCO_3$ are needed, the first fraction of the sulfate ions liberated in this reaction is removed by decantation and further Na_2CO_3-NaOH solution is added to the residue.

REFERENCES:

I. H. N. McCoy. J. Amer. Chem. Soc. 57, 1756 (1935); 59, 1131 (1937); 63, 3422 (1941); J. K. Marsh. J. Chem. Soc. (London) 1943, 531; G. Wilkinson and H. G. Hicks. Phys. Rev. 75, 1370 (1949).

II. R. A. Cooley, D. M. Yost and H. W. Stone in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London; 1946, p. 70; H. N. McCoy. J. Amer. Chem. Soc. 57, 1756 (1935).

III. R. A. Cooley, D. M. Yost and H. W. Stone in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 71.

Pure Ytterbium Compounds

I. ISOLATION OF YTTERBIUM FROM YTTERBIUM EARTHS IN THE FORM OF $YbSO_4$

Reduction of $Yb_2(SO_4)_3$ on a mercury cathode yields $YbSO_4$. The method is particularly suitable for the preparation of pure Yb from ytterbium earth mixtures.

The crude oxide, which must be free of foreign metals [which decrease the overvoltage necessary for the reduction of Yb (*III*) because they tend to form amalgams], is converted to the sulfate by evaporation with H_2SO_4. The electrolyte should contain 120 g. of sulfate and 50 g. of conc. H_2SO_4 per liter. The electrolysis is carried out in a thick-wall beaker *b* (Fig. 285) with its bottom covered with a 1-cm. layer of very pure mercury. A nickel bus bar *k* connects the mercury pool to the negative side of the power supply. A carbon rod *a*, partially immersed in a clay cell *c* filled with dilute H_2SO_4, serves as the anode. A stirrer *r*, which agitates both the mercury surface and the electrolyte, prevents the formation of a dense precipitate on the cathode and thus makes possible the preparation of larger quantities of $YbSO_4$. The electrolyte temperature is maintained at 20°C by external cooling with running water.

The electrolysis is carried out at 72 volts and a current density of 0.05 amp./cm^2 (about 4–4.5 amp. if the beaker is 10 cm. in diameter). At higher current densities the formation of crystals of $YbSO_4$ is so rapid that they occlude considerable quantities of impurity ions (Tm, Lu, etc.) After a few minutes the

solution turns green. When the cathode becomes covered with a loose layer of $YbSO_4$ 2–3 cm. thick, the current efficiency becomes very low and the electrolysis is stopped. Under the conditions described, the process requires 2–3 hours.

The precipitate is collected on a Büchner funnel and washed with water, and the residual water is rapidly removed by suction. Speed is necessary because the oxidation of $YbSO_4$ is accompanied by a marked temperature increase, which could cause decomposition of the product $YbSO_4$ [or $Yb_2(SO_4)_3$].

The precipitate is dissolved in dilute nitric acid, neutralized with ammonia, and reprecipitated with oxalic acid. The oxide obtained upon calcination of the oxalate still contains traces of the sulfate.

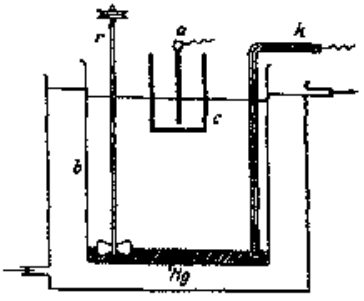

Fig. 285. Electrolytic preparation of ytterbium (II) sulfate. *a* carbon rod, *b* beaker, *c* clay cell.

Additional quantities of $YbSO_4$ may be recovered from the spent electrolyte by inclusion in the isomorphous $SrSO_4$. If this is desired, then the electrolyte should contain only 0.5% H_2SO_4. The $SrSO_4$ solution is prepared by very rapid neutralization of 3 g. of $SrCO_3$ with the stoichiometric quantity of dilute H_2SO_4. This solution is added one hour after the start of the electrolysis. The added solution contains slowly crystallizing $SrSO_4$. The addition is repeated twice at intervals of one hour. After 4–5 hours the precipitate, which contains $SrSO_4$ and $YbSO_4$ in a ratio of about 10:1, is filtered off and washed. The $YbSO_4$ is protected against oxidation to Yb (III) by inclusion in the $SrSO_4$ lattice. On calcination in air, $YbSO_4$ is converted to Yb_2O_3 and may be separated from the $SrSO_4$ by digestion with conc. hydrochloric acid on a water bath. Some additional $SrSO_4$ may be precipitated from this HCl solution by adding dilute sulfuric acid and allowing the solution to stand 12 hours. After removal of the $SrSO_4$, the Yb is precipitated with oxalic acid in the usual manner.

The electrolytic separation of Yb is accompanied by concentration of Tm and Lu in the residual solution.

Europium and samarium may be separated (as $EuSO_4$ and $SmSO_4$) from the other rare earth metals by the same method.

PROPERTIES:

Formula weight 269.11. Green Yb^{2+} ions are oxidized by water to Yb^{3+} (evolution of H_2). Solubility in dilute sulfuric acid:

4 g. $YbSO_4$/liter of 1% H_2SO_4 (0.2N); 8 g. $YbSO_4$/liter of 5% H_2SO_4 (1N); 20 g. $YbSO_4$/liter of 12.5% H_2SO_4 (2.5N). Isomorphous with $SrSO_4$.

II. PURIFICATION OF Yb (Sm, Eu) VIA AN AMALGAM PROCESS

$$Yb^{3+} + 3\,Na(Hg) = Yb(Hg) + 3\,Na^{+}$$

The procedure is suited both for efficient purification of a concentrated ytterbium solution (method *a* below) and for isolation of Yb from a mixture of neighboring rare earths, as well as freeing the latter from Yb (method *b*).

a) A product containing about 97% Yb_2O_3 (balance is ytterbium earths), which may be prepared via $YbSO_4$ by the method described under I, is dissolved in acetic acid on a water bath and evaporated until crystallization. A solution of 107 g. of ytterbium acetate in 133 ml. of boiling water is prepared in a one-liter flask. The hot solution is vigorously shaken for two minutes with 250 ml. of 0.5% sodium amalgam (125% of the theoretical Na). During the reaction 3 ml. of acetic acid is added to prevent the formation of hydroxide (formation of NaOH by partial decomposition of the sodium amalgam). It is best not to shake the mixture until the Na is fully spent, since shaking may cause the Yb to partially redissolve in the form of Yb (II) ions (green color of the aqueous layer). In addition, the Yb content of the amalgam should not exceed 1% to avoid solidification. The amalgam is separated from the solution and water-washed twice to remove the acetate. It is then treated with sufficient dilute hydrochloric acid to neutralize the residual Na. Small quantities of Yb which go into solution during this step are precipitated with NaOH. The amalgam is then shaken with excess hydrochloric acid until calomel starts to form. The $Yb(OH)_3$ precipitate is added to the HCl solution and the mixture is evaporated to a sirup. The precipitating NaCl is filtered off. The filtrate is calcined. Spectroscopically pure Yb_2O_3 is obtained in a yield exceeding 90%.

The acetate solution remaining from the first extraction may be allowed to react, after addition of 3 ml. of acetic acid, with an additional 83 ml. of sodium amalgam. The resultant ytterbium amalgam is worked up as above. The mother liquor is converted to the hydroxide and may be reextracted after dissolving in acetic acid.

b) If complete extraction of Yb from a mixture of ytterbium earths is desired, the solution must be shaken up to 20 times with sodium amalgam and the aqueous layer repeatedly freed of the sodium acetate formed, since high concentrations of the latter interfere with the reaction. Using this method, Marsh was able to reduce the Yb content of a Lu preparation to 0.0033%.

Pure compounds of Sm and Eu may be prepared by a basically similar method. The preferential formation of Sm, Eu and Yb amalgams is due to the fact that metallic Eu and Yb always form divalent ions, while Sm does so partially.

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I. A. Brukl. Angew. Chem. 50, 25 (1937); 49, 159 (1936); W. Kapfenberger. Z. anal. Chem. 105, 199 (1936); J. K. Marsh. J. Chem. Soc. (London) 1937, 1367.
II. J. K. Marsh. J. Chem. Soc. (London) 1942, 398, 523; 1943, 8, 531; T. Moeller and H. E. Kremers. Ind. Eng. Chem., Anal. Edit. 17, 798 (1945).

Metallic Rare Earths

I. REDUCTION OF THE CHLORIDES WITH METALS

LANTHANUM METAL, POWDER

$$\underset{245.3}{LaCl_3} + \underset{117.3}{3\,K} = \underset{138.9}{La} + \underset{223.7}{3\,KCl}$$

DropBooks

The Vycor (or similar glass) apparatus shown in Fig. 286 is dried by fanning with a flame under high vacuum. A vacuum pump is connected at *d*; *c* and *i* are closed off with rubber stoppers. The apparatus is filled with pure, dry nitrogen or argon, and a small tube containing distilled potassium is placed in tube *b*; the neck of the potassium ampoule is broken immediately prior to use. Anhydrous rare earth chloride is introduced into *a* through tube *c* (air must be excluded during this operation) and tube *c* is immediately closed off again. The apparatus is melt-sealed at *c* and *i*, and evacuated through *d* to a high vacuum. Capillary *f* is heated and bent downward (to position *b'*) and the potassium is slowly distilled from *b'* into *g*. This second distillation removes the possibility of traces of potassium oxide coming into contact with the chloride. The apparatus is then melt-sealed at *f* and *e*, a small portion of the potassium is distilled into constriction *h*, and the tube (*a*–*g*) is heated to 220–350°C in an electric furnace. Part of the rare earth chloride is reduced after a short time; an additional fraction of the potassium is then distilled into *h*, and the tube is reheated in the furnace. This stepwise reduction is continued until most of the rare earth chloride has been converted to the metal. Only then is the remaining potassium distilled by turning the tube upside down and placing almost the entire apparatus (*f*–*a*) in the furnace. The potassium is then immediately distilled off

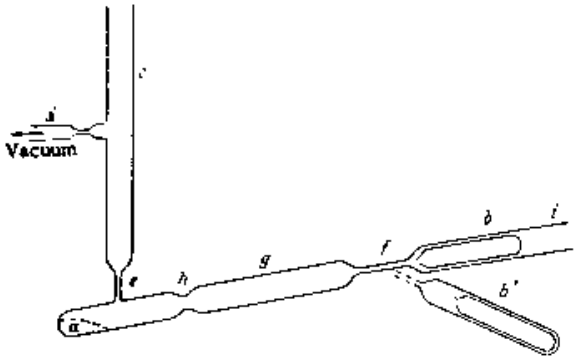

Fig. 286. Preparation of metallic rare earths by reduction of the chloride with metallic potassium. *a* rare earth chloride; *b*, *b'* metallic potassium; *c* filling tube for the rare earth chloride; *d* connection to vacuum pump.

again, and the process is repeated several times. This stepwise reduction prevents the reactants from fusing together, and thus ensures completion of the reaction. Finally the tube is gradually pulled out of the furnace, until a potassium mirror no longer forms at the unoccupied spots on the tube between *g* and *h*. The product consists of a loose black powder which does not adhere to the glass walls of the tube.

After cooling, tip *f* is connected via a dry rubber tube to the vacuum–N_2 (or Ar) system and broken off under N_2 or Ar. The alkali metal at *g* serves as a barrier and traps any traces of water vapor which may be introduced. The tube can now be broken at *h* without endangering the product, and the mixture of rare earth metal + 3 alkali chloride at *a* may be poured into a transfer apparatus through which protective gas is flowing (for transfer apparatus see Part I, p. 75 ff., especially Fig. 54).

All the rare earth metals, in the form of powders mixed with alkali chloride, may be prepared by this method. In preparing Sm, Eu or Yb metals (these elements form divalent compounds), a temperature of 250°C must not be exceeded, since at higher temperatures, the direction of the reaction is reversed and $SmCl_2$, $EuCl_2$ and $YbCl_2$ are formed.

CERIUM METAL, SOLID

$$\underset{493.0}{2\,CeCl_3} + \underset{120.3}{3\,Ca} = \underset{280.3}{2\,Ce} + \underset{333.0}{3\,CaCl_2}$$

A crucible of sintered CaO or dolomite is placed in an iron tube provided with a welded-on bottom and a screw lid, and the space

between the crucible and the tube is filled with CaO powder. This precaution prevents contact between the reaction mixture and the iron wall if the crucible should break. Since the heat of the reaction between Ca and $CeCl_3$ is not sufficient for clean separation between the metal ingot and the slag, it is necessary to add a third component which produces a highly exothermic reaction with Ca, e.g., I_2, S, $KClO_3$ or $ZnCl_2$.

For a tube 20 cm. high and 2.5 cm. in diameter, suitable quantities of reactants are 200 g. of $CeCl_3$, 103 g. of I_2 (mole ratio $I:CeCl_3 = 0.625:1.0$) and a 15% excess of very pure Ca powder (particles 0.3–2 mm.). The reactants are mixed under anhydrous condition and placed in the crucible; the iron cap is filled with CaO and screwed on. The tube is placed in a furnace heated to 650–750°C. The reaction starts suddenly when the temperature inside the tube reaches 400°C. The yield of Ce metal is 93%. The reaction may be carried out on a larger scale, but due to smaller relative heat losses, only 0.5 mole of I_2 per mole of $CeCl_3$ and a 10% excess of Ca are needed. The use of sulfur or $KClO_3$ lowers the yield. The resultant Ce metal contains 1–5% Ca and 0.1–1% Mg.

When smaller quantities of raw materials are used, the reaction temperature must be increased. This is done by replacing the iodine with $ZnCl_2$ (3–6% Zn, based on the amount of Ce). The product is freed of zinc by evaporating it in vacuum. The yield is 90% of Ce containing only 0.002% Zn.

Any Ca, Mg or Zn which may be dissolved in the Ce is removed by placing the product in a crucible made of MgO, CaO, BeO or Ta, which in turn is placed in a second crucible made of graphite. This assembly is placed in a quartz tube with one end closed and the other connected to a high-vacuum pump via a water-cooled brass coupling. The coupling is provided with a glass window to facilitate optical temperature measurement. The well-insulated quartz tube is placed for 30 minutes in an induction furnace heated to 1250°C. The melt is held at this temperature for 10–15 minutes, until cessation of bubbling.

This entire sequence of procedures can be used to prepare La, Ce, Pr and Nd in 99.9% purity. The reaction with Ca converts $SmCl_3$, $EuCl_3$ and $YbCl_3$ to the dichlorides. The preparation of Y fails due to the high melting point of this metal.

II. REDUCTION OF THE OXIDES WITH METALS

SAMARIUM METAL, SOLID

A tantalum crucible (height 20 cm., diameter 2.5 cm.) containing a mixture of 20 g. of Sm_2O_3 and 20 g. of freshly prepared La turnings is heated for 30 minutes at 1450°C in an electric furnace at a pressure of 0.001 mm. The upper part of the crucible projects

from the furnace and is closed off with a lid carrying a connection to a high-vacuum pump. The Sm is deposited on the cooler parts of the crucible. The method results in a highly pure metal free of La; the yield is 80%.

Pure Yb metal may be prepared by the same method. In a similar preparation the La may be replaced by Ca or Al.

PROPERTIES:

Atomic weight 150.35. Silvery, air-stable metal. More volatile than La metal.

REFERENCE:

A. Jandelli. Atti Reale Accad. Naz. Lincei, Rend. VIII 18, 644 (1955).

III. ELECTROLYSIS OF FUSED CHLORIDES

LANTHANUM METAL, SOLID

The apparatus for melt electrolysis is shown in Fig. 287. The anode is a graphite crucible (inside diameter 40 mm., inside height 80 mm., wall thickness 5 mm., bottom thickness 10 mm.) containing the melt. The current is supplied through a sleeve surrounding the bottom of the crucible; the sleeve is connected to the power supply through an iron rod. The cathode is a Mo rod (diameter 10 mm., length about 100 mm.) friction-fitted into an iron pipe and covered near the top with a tube of sintered corundum cemented in with a talc-waterglass mixture. The rotating cathode should be able to agitate the melt; the current is supplied via a carbon friction contact. To collect the La metal which is thrown off by the spinning cathode and protect it against contact with graphite and the Cl_2 formed at the anode, a sintered alumina crucible (upper diameter 40 mm., height 30 mm.) is fitted exactly into the graphite crucible.

The furnace is heated to 1000°C and the crucible is charged with a salt mixture of the following composition: 27.4% $LaCl_3$, 68.0% KCl, 4.6% CaF_2 (3.75 g. of KCl and 0.25 g. of CaF_2 per gram of La_2O_3). It is advisable to add initially only a small portion of the fluxing material. The mixture is allowed to melt and any NH_4Cl present is allowed to escape; the remainder of the flux is then added during the first minutes of the actual electrolysis. The electrolysis is run at 6–8 volts and 40 amp. The highest current efficiencies and product yields are obtained at about 7 amp. per $cm.^2$ and 25 amp.-hr. The cathode should rotate at a rate of 1–2 r.p.s. At the end of the reaction, the current is shut off and stirring (rotation of the cathode) is continued for a few minutes. The crucible is then removed, allowed to cool and broken

to pieces. The resultant ingot contains more than 99% lanthanum.

With some of the other rare earth metals (Sc, Gd), it is necessary to work below the melting point of the metal. In such cases the metal is deposited on a cathode of molten Zn or Cd, in which the metal dissolves. The Zn or Cd is vacuum-distilled from the product alloy.

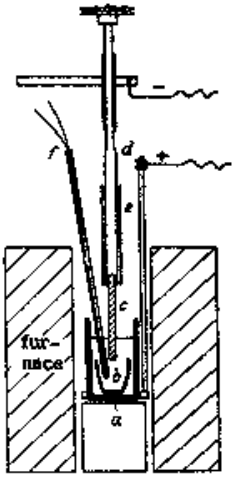

Fig. 287. Preparation of lanthanum metal. *a* graphite crucible; *b* corundum crucible; *c* molybdenum electrode; *d* iron rod; *e* corundum protective tube; *f* thermocouple.

PROPERTIES:

Atomic weight 138.92. Iron gray, with a vivid metallic luster when polished; ductile, malleable. Tarnishes rapidly in moist air. M.p. 885°C; d^{20} 6.18. Crystal structure: α-La, type A3 (Mg type); β-La, type A1 (Cu type).

DropBooks

CERIUM METAL, SOLID

Metallic cerium is obtained via electrolysis of a fused mixture of anhydrous $CeCl_3$ and KCl–NaCl.

The reaction is carried out in a roughly cylindrical copper vessel, with a wall thickness of 1 mm. (see Fig. 260, p. 957). The inside diameter is about 2.5 cm. At the top, the tube widens to an inverted truncated cone with a base diameter of about 8 cm. The cathode is a carbon rod (diameter 9 mm., length 16 cm.) inserted from below; up to about 1.5 cm. from the upper end of the cylindrical section of the tube, the cathode is wrapped with asbestos cord; this asbestos cord, in conjunction with the unmelted portion of the chloride mixture which rests on it, serves as the bottom of the melting pot. The anode is a somewhat thicker carbon rod inserted from above. The position of the anode may be adjusted by a height-regulating device attached to the side of this crucible. The electrode gap is located approximately at the midheight of the conical melting space.

For small-scale preparations, a thin carbon rod about 3 mm. in diameter and 20 mm. long is clamped between the two cathodes. The crucible is filled with 200 g. of $CeCl_3$ and 15–20 g. of KCl–NaCl (equimolar mixture) and the crucible contents are melted as rapidly

as possible with a current of 30–40 amp. at 12–15 volts. As soon as the melt thins in consistency, the anode is raised somewhat, the thin carbon rod is removed, and electrolysis is carried out for several hours at 700–750°C. After solidification the metallic ingot is removed and remelted under KCl-NaCl in a silicon carbide crucible.

PROPERTIES:

Atomic weight 140.13. Iron gray, with a vivid metallic luster when polished; may be cut with a knife; somewhat harder than lead; ductile, malleable. M.p. 635°C; d^{25} 6.92. Tarnishes rapidly in moist air; burns at 160–180°C in a stream of O_2. Attacked by water (evolution of H_2). Crystal structure: α-Ce, type A3 (Mg type); β-Ce, type A1 (Cu type).

IV. ELECTROLYSIS OF ALCOHOLIC CHLORIDE SOLUTIONS

The electrolysis of an alcoholic solution of a rare earth chloride on a mercury cathode (20 volts, current density 0.02 amp./cm^2) yields an amalgam with a rare earth metal concentration of up to 3%. The mercury is removed by vacuum distillation, leaving behind the pure rare earth metal.

REFERENCES:

I. W. Klemm and H. Bommer. Z. anorg. allg. Chem. 231, 141 (1937); H. Bommer and E. Hohmann. Ibid. 248, 359 (1941); F. H. Spedding et al. Ind. Eng. Chem. 44, 553 (1952); F. H. Spedding and A. H. Daane. J. Amer. Chem. Soc. 74, 2783 (1952); E. J. Onstott. Ibid. 75, 5128 (1953).

II. A. H. Daane, D. H. Dennison and F. H. Spedding. J. Amer. Chem. Soc. 75, 2272 (1953); E. J. Onstott. Ibid. 77, 812 (1955).

III. F. Weibke and J. Sieber. Z. Elektrochem. 45, 518 (1939); F. Trombe. Bull. Soc. Chim. France (5) 2, 660 (1935); W. Fischer, K. Brünger and H. Grieneisen. Z. anorg. allg. Chem. 231, 54 (1937); W. Muthmann et al. Liebigs Ann. 320, 242 (1901); see also Ind. Eng. Chem. 3, 880 (1911).

IV. V. B. S. Hopkins et al. J. Amer. Chem. Soc. 57, 2185 (1935); 56, 303 (1934); 53, 1805 (1931); Z. anorg. allg. Chem. 211, 237 (1933).

Rare Earth Trichlorides

LnCl$_3$ (anhydrous)

I. REACTION OF THE OXIDES WITH Cl_2 AND S_2Cl_2

The rare earth oxide (1–2 g.) is placed in a porcelain boat and chlorinated for about five hours in a stream of Cl_2-S_2Cl_2 (prepared

by bubbling Cl_2 through a wash bottle filled with S_2Cl_2 and standing in a 30–40°C water bath). The temperature is slowly raised during the process from an initial 400°C to about 20° below the melting point of the chloride. The chlorides deposit on the bottom as loose powders ready for use in further reactions.

The chlorides of Sm, Eu, Gd, Tb, Dy and Y, which melt below 700°C, are best prepared by dehydration of the hydrated chlorides in a stream of HCl.

II. DEHYDRATION OF THE HYDRATED CHLORIDES IN A STREAM OF HCl

The hydrate of the rare earth chloride (3–5 g.) is dried in a vacuum desiccator and then heated by stages in the region of the individual hydrate transition temperature while a stream of oxygen-free N_2–HCl mixture is passed over it. The boat, which may be of porcelain, quartz, gold or platinum, is placed in a tube of Pyrex, Vycor or quartz. The temperature may be raised beyond the transition region only when no further hydrochloric acid condenses on those sections of the tube which project from the furnace; if this precaution is not observed the chloride melts in the water of crystallization and the product then contains oxychlorides. Dehydration is complete after 30–60 hours. Heating at 300–400°C in a stream of pure HCl is continued for one hour, and the product is allowed to cool in a stream of N_2. The stopcocks and ground joints which come into contact with the hydrogen halides are greased with a mixture of paraffin and paraffin oil.

The product must yield a clear solution in water. Contamination with traces of oxychloride may be recognized by turbidity of the aqueous solutions.

III. HEATING OF THE HYDRATED CHLORIDES WITH NH_4Cl

Dehydration of the hydrated chlorides may also be achieved by heating with an excess (1–1.5 times) of NH_4Cl. The products, however, always contain small quantities of NH_4Cl.

IV. HEATING OF THE OXIDES WITH NH_4Cl

A 250-ml. quartz Erlenmeyer flask equipped with an adapter that can be closed off with a small glass cap and can also be connected to a quartz tube (length 25 cm., diameter 3 cm.) is filled with a mixture of 60 g. of the rare earth oxide and 120 g. of NH_4Cl.

The flask, tilted about 30° from the horizontal, is slowly rotated around its axis and heated to 220–250°C on an air bath. Evolution of NH_3 ceases after 6–8 hours. After a short cooling

period, the flask is closed with the glass cap while still warm and then allowed to cool completely. The cap is then replaced with the quartz tube. The other end of the tube is connected (via two gas traps) to an oil vacuum pump. The flask is evacuated and surrounded with an electric furnace extending a few centimeters beyond the quartz joint. The mixture is slowly heated to 300–350°C, resulting in evolution of a small quantity of water vapor and NH_3. The excess NH_4Cl sublimes into the quartz tube. To prevent cracking of the glass connection, it is sometimes necessary to cool the other end of the tube with a water-cooled lead or tin coil. After 4–5 hours, the mixture is allowed to cool, the quartz tube is cleaned, and the sublimation is repeated. Complete removal of the last traces of NH_4Cl is attained only at 400°C.

The method is particularly suited to the preparation of large quantities of product. The oil pump may be replaced by a jet ejector if an adequate trap filled with a drying agent is inserted in the line.

The above methods are suitable for the preparation of all the anhydrous rare earth chlorides, including that of yttrium. For the preparation of $ScCl_3$, see W. Fischer, R. Gewehr and H. Wingchen, Z. anorg. allg. Chem. 242, 170 (1939).

PROPERTIES:

Hygroscopic powders which give clear solutions in water and alcohol. The melting points drop from $LaCl_3$ (~860°C) to $TbCl_3$ (~600°C) and rise again to $LuCl_3$ (~900°C).

REFERENCES:

I. W. Klemm, K. Meisel and H. U. von Vogel. Z. anorg. allg. Chem. 190, 123 (1930).
II. O. Hönigschmid and H. Holch. Z. anorg. allg. Chem. 165, 294 (1927); 177, 94 (1928); L. Holleck. Angew. Chem. 51, 243 (1938).
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IV. A. Brukl. Angew. Chem. 52, 152 (1939); J. B. Reed. J. Amer. Chem. Soc. 57, 1159 (1935); D. H. West and B. S. Hopkins. Ibid. 57, 2185 (1935).

Rare Earth Tribromides

$LnBr_3$ (anhydrous)

I. DEHYDRATION OF HYDRATED BROMIDE-NH_4Br MIXTURES IN A STREAM OF HBr

A hydrobromic acid solution containing six moles of NH_4Br per mole of the rare earth bromide is carefully evaporated to dryness

on an air bath, with constant stirring toward the end of the operation. The evaporation should be carried out in a stream of CO_2. The crumbly salt mixture is dehydrated in a stream of HBr at slowly increasing temperatures. The product must not be allowed to melt under any circumstances! The sublimation of NH_4Br starts at 250°C; its last traces are removed at 600°C.

Very pure tribromides are obtained by dehydration and removal of NH_4Br from the $LnBr_3 \cdot 6\ H_2O$-NH_4Br mixture on heating in high vacuum. For the preparation of $ScBr_3$, see W. Fischer, R. Gewehr and H. Wingchen, Z. anorg. allg. Chem. 242, 170 (1939).

II. TREATMENT OF THE ANHYDROUS CHLORIDES WITH HBr

The anhydrous rare earth chloride (1-2 g.) is heated in a stream of HBr for about seven hours. The temperature is slowly raised from 400°C to slightly below the melting point of the bromide.

PROPERTIES:

Hygroscopic powders. The melting points rise with atomic weight from $SmBr_3$ (~628°C) to $ErBr_3$ (~950°C).

REFERENCES:

I. G. Jantsch et al. Z. anorg. allg. Chem. 207, 361 (1932); G. Jantsch and N. Skalla. Ibid. 201, 213 (1931).
II. W. Klemm and J. Rockstroh. Z. anorg. allg. Chem. 176, 189 (1928).

PrepBooks

Rare Earth Triiodides

LnI_3 (anhydrous)

I. DEHYDRATION OF HYDRATED IODIDE-NH_4I MIXTURES IN A STREAM OF HI-H_2

A mixture of one mole of $LnI_3 \cdot 6\ H_2O$ and six moles of NH_4I is heated in a stream of HI + H_2 mixture with a moderate HI concentration. Under no circumstances should the temperature be raised at a rate fast enough to melt or sinter the product during the dehydration. Because the product is extremely sensitive to O_2 and moisture, great care must be exercised in purifying the gases. Since the last traces of NH_4I sublime only at high temperatures, the mixture is heated to 600°C during the last stage. When the dehydration is complete, the HI is flushed out with N_2. The iodides are stored under N_2.

This method is suitable for the iodides of La, Pr and Nd. However, SmI_3 is usually contaminated with some SmI_2, which is

converted to SmI_3 after elimination of the NH_4I. This is done by heating the product to 500°C and treating it with iodine vapor. Again, under the conditions of this method, EuI_3 decomposes to EuI_2 and iodine. Because of their tendency to hydrolyze, the iodides of the rare earth metals which are less electropositive than Eu can be prepared only from the anhydrous chlorides. The same applies to CeI_3.

II. REACTION OF THE ANHYDROUS CHLORIDES WITH MIXTURES OF HI - H_2

The anhydrous rare earth chloride is heated for 4-6 hours until 600°C is reached; it is then held at this temperature for 30-40 hours in a stream of HI-H_2 containing as much HI as possible. The iodides are cooled and stored under N_2.

Special care must be exercised with the lower-melting chlorides, since the chlorides no longer react with the HI when enveloped in iodide.

PROPERTIES:

Hygroscopic powders. The melting points drop from LaI_3 (~761°C) to PrI_3 (~733°C) and rise again to LuI_3 (~1045°C).

REFERENCES:

I. G. Jantsch et al. Z. anorg. allg. Chem. 185, 56 (1930); E. Hohmann and H. Bommer. Ibid. 248, 384 (1941).
II. G. Jantsch et al. Z. anorg. allg. Chem. 201, 207 (1932); 207, 353 (1932); 212, 65 (1933); E. Hohmann and H. Bommer. Ibid. 284, 383 (1941).

Rare Earth Dihalides

LnX_2 (anhydrous)

The trihalides of Sm, Eu and Yb are converted to the dihalides by heating in a stream of carefully purified H_2. The temperature should not be raised as high as the melting point of the trihalide, since the molten compounds react either slowly or not at all with H_2.

All the dichlorides, dibromides and diiodides of Sm, Eu and Yb can be prepared by this method. Note that EuI_2 is formed under the conditions given for the preparation of the triiodides (method II). Thermal degradation of YbI_3 in high vacuum is the preferable method for obtaining YbI_2.

REFERENCES:

W. Prandtl and H. Kögl. Z. anorg. allg. Chem. 172, 265 (1928); G. Jantsch, H. Rüpnig and W. Runge. Ibid. 161, 210 (1927); W. Kapfenberger. Ibid. 238, 281 (1938); G. Jantsch, N. Skalla and H. Jawurek. Ibid. 201, 218 (1931).

Cerium (III) Oxide

Ce_2O_3

Reduction of CeO_2 in a stream of H_2 is the best method. It is carried out in a silicon carbide boat. The H_2 must be carefully purified (free of oxygen) and dried. Very pure CeO_2 (3 g.), prepared as described on p. 1133, requires about 80 hours at 1000°C (or 45 hours at 1100°C) for complete reduction. Traces of La and Nd moderately increase the rate of reduction, while Pr and Tb do so markedly. The reduction is complete when the blue-black color of the partially reduced intermediates changes to the pure golden yellow of Ce_2O_3.

PROPERTIES:

Golden yellow (greenish yellow products are incompletely reduced); converts slowly in air to CeO_2; rapid conversion, accompanied by a glow, on slight heating. Readily soluble in acids. d (x-ray) 6.856. Crystal structure: type $D5_3$ (A-sesquioxide type).

DropBooks

REFERENCES:

E. Friederich and L. Sittig. Z. anorg. allg. Chem. 134, 316 (1925); 145, 127 (1925); W. Zachariasen. Z. phys. Chem. 123, 134 (1926); G. Brauer and U. Holtschmidt. Z. anorg. allg. Chem. 265, 105 (1951); U. Holtschmidt. Thesis, Freiburg i. Br., 1952; G. Brauer and U. Holtschmidt. Z. anorg. allg. Chem. 279, 129 (1955); D. J. M. Bevan. J. Inorg. Nuclear Chem. 1, 49 (1955).

Praseodymium (IV) Oxide

PrO_2

At 400°C, praseodymium oxide preparations achieve a composition corresponding to PrO_2 only under an O_2 pressure of 282 atm. However, at 300°C, only 50 atm. of O_2 suffices. The oxidation

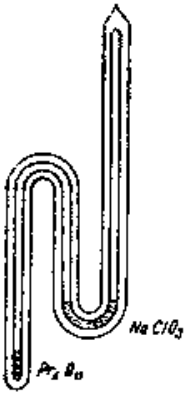

Fig. 288. Quartz tube for oxidation of praseodymium oxide.

Pr_6O_{11} is carried out in the quartz tube shown in Fig. 288. The O_2 is generated by the decomposition of a weighed amount of $NaClO_3$ in the sealed tube. The amount of chlorate used is calculated beforehand to yield an O_2 pressure of 50 atm. in the sealed tube. After the $NaClO_3$ is decomposed by local heating, the entire tube is heated to 300°C for 48 hours.

PROPERTIES:

Dark brown powder, easily reduced by H_2 to Pr_2O_3. Crystal structure: type C1 (CaF_2 type). Measurements of the dissociation pressure of O_2 indicate that the Pr-O system contains additional stable phases with compositions of $PrO_{1.715}$, $PrO_{1.802}$ and $PrO_{1.833}$.

REFERENCES:

J. D. McCullough. J. Amer. Chem. Soc. 72, 1386 (1950); W. Simon and L. Eyring. Ibid. 76, 5872 (1954); R. E. Ferguson, E. D. Guth and L. Eyring. Ibid. 76, 3890 (1954).

Rare Earth Hydroxides

$Ln(OH)_3$ (crystalline)

Crystalline trihydroxides $Ln(OH)_3$ of the lanthanides (at least those ranging from La to Er) and of Y are prepared by heating the hydroxides under conc. (7N) NaOH: A solution of 2 g. of the nitrate in 2 ml. of water is added to a silver crucible containing a solution of 7 g. of NaOH in 7 ml. of water. The crucible, covered with a silver lid, fits precisely into a pressure tube closed off with a screwed-on cap. The tube is heated for 25 hours at 200°C. The mixture is cooled, the clear supernatant is siphoned off, and the product is washed several times (by decantation) with CO_2-free water; it is then washed on a filter crucible in the absence of CO_2 and dried by suction. Final drying is achieved by storing the product for 24 hours over conc. H_2SO_4 in a vacuum desiccator.

PROPERTIES:

Transparent, hexagonal prisms. Solubility in conc. NaOH increases with the atomic number. The dehydration passes through

an intermediate stage, MO(OH), in which the compounds have the PbFCl structure. $La(OH)_3$ has UCl_3 structure.

REFERENCES:

R. Fricke and A. Seitz, Z. anorg. allg. Chem. 254, 107 (1947); R. Roy and H. A. McKinstry, Acta Crystallogr. (Copenhagen) 6, 365 (1953).

Lanthanum Sulfide

La_2S_3

$$\underset{490.6}{2\,LaCl_3} + \underset{102.2}{3\,H_2S} = \underset{374.0}{La_2S_3} + \underset{218.8}{6\,HCl}$$

Anhydrous $LaCl_3$ is heated in a stream of pure H_2S. The temperature is maintained at 500–600°C for several hours, followed by heating at 600–700°C overnight. Prior to use, the H_2S is dried over $CaCl_2$ and P_2O_5, liquefied at −78°C (see p. 344 ff.) and evaporated from the liquid [A. Simon, Ber. dtsch. chem. Ges. 60, 568 (1927) and this Handbook, Part I, p. 46 ff.] at a flow rate of one bubble per second. The intermediate product is then heated to 800–1000°C for several hours and allowed to cool in a stream of H_2S.

This method is suitable for all the rare earth sulfides, including those of Sc and Y.

$$\underset{566.0}{La_2(SO_4)_3} + \underset{409.0}{12\,H_2S} = \underset{374.0}{La_2S_3} + \underset{384.8}{12\,S} + \underset{216.2}{12\,H_2O}$$

The recrystallized sulfate hydrates may also serve as starting materials. Except for the fact that the decomposition temperatures of the dehydrated sulfates (given by Brill; see references below) are different, the procedure is similar to that given above for the chlorides. In this case, however, the products are usually contaminated with variable amounts of Ln_2O_2S.

Under these conditions $Y_2(SO_4)_3$ and $Er_2(SO_4)_3$ form Ln_2O_2S exclusively. It is also possible to prepare La_2O_2S by reduction of $La_2(SO_4)_3$ with H_2 at 800°C.

If the treatment with H_2S is carried out at a lower temperature (580–600°C), the sulfates of La, Ce and Pr form polysulfides Ln_2S_4, which decompose above 600°C to Ln_2S_3 and S.

The anhydrous rare earth sulfates start to decompose above 600°C, yielding the basic sulfates $Ln_2O_3 \cdot SO_3$, whose decomposition temperatures decrease from La (1150°C) to Yb (900°C).

DropBooks

PROPERTIES:

Light yellow to light orange, opaque, hexagonal prisms. d^{35} 4.86.

REFERENCES:

I. W. Klemm, K. Meisel and H. U. von Vogel. Z. anorg. allg. Chem. 190, 123 (1930).
II. O. Brill. Z. anorg. allg. Chem. 47, 464 (1905); W. Biltz. Ibid. 71, 424 (1911); Ber. dtsch. chem. Ges. 41, 3341 (1908).

Lanthanum Selenides

La_2Se_3, La_2Se_4

$$\underset{325.8}{La_2O_3} + 3\,\underset{242.9}{H_2Se} = \underset{514.7}{La_2Se_3} + 3\,\underset{54.0}{H_2O}$$

I. Both La_2Se_3 and La_2Se_4 are prepared by high-temperature reaction of the oxide or chloride with H_2Se.

A boat with La_2O_3 is placed inside a quartz tube surrounded by an electric furnace. Several boats containing Se are placed ahead of the oxide and heated with Bunsen burners to a temperature at which the Se slowly evaporates. A stream of carefully purified H_2 is passed through the quartz tube. After treatment for about five hours, during which the temperature of the La_2O_3 is slowly raised from 600 to 1000°C, La_2Se_4 is obtained in quantitative yield.

Heating the polyselenide for 30–60 minutes in high vacuum at 600–800°C yields La_2Se_3. This operation must be carried out in a porcelain or corundum boat, since quartz reacts to form the rare earth oxide and $SiSe_2$.

The same procedure is used for Ce_2Se_4 and Pr_2Se_4. However, Nd yields only $Nd_2Se_{3.5}$. The other rare earths do not form polyselenides. The sesquiselenides of these elements are best prepared by treating the rare earth chlorides with H_2Se:

$$\underset{277.8}{2\,La} + \underset{236.9}{3\,Se} = \underset{514.7}{La_2Se_3}$$

II. Synthesis from the elements by heating a stoichiometric mixture in a silicon carbide crucible held in an evacuated, sealed quartz tube.

PROPERTIES:

La_2Se_3: Brick red. Insoluble in both cold and boiling water; violently evolves H_2Se in dilute acids; decomposes slightly after several days in moist air. d^{20} 6.19.

REFERENCES:

I and II: W. Klemm and A. Koczy. Z. anorg. allg. Chem. 233, 86 (1937); A. Koczy. Thesis, Danzig, 1936.

La, Ce, Pr and Nd Monochalcogenides

LnS, LnSe, LnTe

These compounds are prepared by synthesis from the elements. The rare earth metal powder, as pure as possible, is placed in one of the arms of an L-shaped glass tube. The other arm contains the stoichiometric quantity of S, Se or Te (1:1 ratio). The tube is melt-sealed in vacuum and heated in an electric furnace until the non-metal is completely consumed. The temperature should reach 400–450°C by the end of 2–3 days. Powder pattern analysis of the products indicates the formation of nonhomogeneous materials containing Ln_2X_3 and Ln_3X_4, but not LnX, which starts to form at 1000–1100°C.

For this reason, the samples obtained at the lower temperature are compressed (10 tons/cm.^{2}) to cylindrical tablets in an atmosphere of CO_2 and sealed (under vacuum) in quartz tubes. The material is then slowly heated to 1000°C in an electric furnace (to 1100°C in the case of the tellurides). The products are 99.2–99.5% pure.

In addition, CeS may be prepared by heating Ce_2S_3 to 2200°C with a small excess of CeH_3; an evacuated molybdenum container is used.

PropBooks

PROPERTIES:

The monosulfides of La, Ce, Pr and Nd are greenish yellow, the monoselenides reddish yellow, the monotellurides blue violet. The sulfides decompose in moist air to form H_2S. Crystal structure: type B1 (NaCl type).

REFERENCES:

A. Jandelli. Gazz. Chim. Ital. 85, 881 (1955); E. O. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and L. N. Lofgren. J. Amer. Chem. Soc. 72, 2249 (1950).

Europium (II) Chalcogenides

EuS, EuSe, EuTe

$$EuCl_2 + S\,(Se; Te) + H_2 = EuS\,(EuSe; EuTe) + 2\,HCl$$

222.8 32.1 (79.0; 127.6) 2.0 184.0 (230.9; 278.5) 72.9

A mixture of $EuCl_2$ with a severalfold excess of S, Se or Te is heated for several hours to 600°C in a fast stream of purified H_2

This produces the desired chalcogenides. The S, Se or Te in excess of the desired composition is removed by heating for a few hours more at 820°C in the stream of H_2.

Europium also forms an oxide, EuO, which may be prepared by heating Eu_2O_3 with La or C.

PROPERTIES:

EuO: dark red or blue depending on the conditions of preparation; d 7.7. EuS: blue black; d 5.7. EuSe: brown black; d 6.4. EuTe: black, metallic appearance. All the Eu (II) chalcogenides crystallize in type B1.

REFERENCES:

W. Klemm and H. Senff. Z. anorg. allg. Chem. 241, 259 (1939); H. A. Eick, N. C. Baenziger and L. Eyring, J. Amer. Chem. Soc. 78, 5147 (1956); M. Guittard and A. Benacerraf. Comptes Rendus Hebd. Séances Acad. Sci. 248, 2589 (1959); L. Domange, J. Flahaut and M. Guittard. Ibid. 249, 697 (1959); J. C. Achard. Ibid. 250, 3025 (1960).

Rare Earth Sulfates

$$Ln_2(SO_4)_3 \cdot nH_2O$$

The oxide (0.3 g.) is dissolved in 20 ml. of hot 6N H_2SO_4. The solution is filtered and allowed to crystallize over conc. H_2SO_4 in a vacuum desiccator. The product is filtered through fritted porcelain, washed twice with 10 ml. of water and once with 10 ml. of ethanol, and dried in air for four hours.

The product obtained from La by this procedure is $La_2(SO_4)_3 \cdot 9H_2O$ and from Yb it is $Yb_2(SO_4)_3 \cdot 11H_2O$. The remaining rare earths and yttrium yield octahydrates.

Cerium sulfate, $Ce_2(SO_4)_3 \cdot 5H_2O$, is prepared by heating 3 g. of the chloride with 5 ml. of conc. H_2SO_4 until all the hydrogen chloride has been removed. Then 20 ml. of water is added and the product is allowed to crystallize in a desiccator.

Alternate method: A neutral or slightly acid solution of the sulfate is treated with about 3/4 of its volume of ethanol. The sulfates may thus be isolated rapidly and quantitatively, without the evaporation stage.

Anhydrous rare earth sulfates may be prepared by dehydration of the hydrates at 400–600°C. The same procedure can also be used with the acid sulfates obtained by evaporating the chlorides with conc. H_2SO_4.

PROPERTIES:

The rare earth sulfates usually crystallize as octahydrates. The anhydrous sulfates are formed in the range of 155 to 295°C; if the dehydration is carried out carefully, it is sometimes possible to detect intermediate stages, such as pentahydrates (Pr, Nd, Er) and dihydrates (La, Ce, Nd, Yb).

REFERENCES:

W. W. Wendlandt. J. Inorg. Nuclear Chem. 7, 51 (1958); W. Biltz. Z. anorg. Chem. 17, 427 (1911); O. Brill. Z. anal. Chem. 47, 464 (1905).

Rare Earth Nitrides

LnN

Rare earth nitrides may be prepared by heating the metal in a stream of N_2 or NH_3, or by reaction of the chloride with NH_3. The preparation of LaN by the first method is given as an example.

LANTHANUM NITRIDE, LaN

Lanthanum filings (several hundred milligrams), prepared from the metal in a stream of N_2, are freed of iron with a magnet and heated in a molybdenum boat placed in a stream of purified N_2. The azotization requires 2-4 hours at 750°C, 1-2 hours at 900°C.

The nitrides of Ce, Pr, Nd, Sm, Eu and Yb may be prepared by a basically similar method.

PROPERTIES:

Black powder; evolves NH_3 in moist air. Crystal structure: type B1 (NaCl type).

REFERENCES:

B. Neumann, C. Kröger and H. Haebler. Z. anorg. allg. Chem. 207, 148 (1932); W. Muthmann and H. Kraft. Liebigs Ann. 325, 274 (1902); A. Jandelli and E. Botti. Atti R. Acad. Naz. Lincei, Rend. [6] 25, 129 (1937); R. A. Young and W. T. Ziegler. J. Amer. Chem. Soc. 74, 5251 (1952); H. A. Eick, N. C. Baenziger and L. Eyring. Ibid. 78, 5987 (1956); B. M. Ormont and E. V. Balabanovich. Russian Patent 51,424, Chem. Zentr. 1938, II, 573; W. Klemm and G. Winkelmann. Z. anorg. allg. Chem. 288, 87 (1956).

DropBooks

Rare Earth Nitrates

$Ln(NO_3)_3$ (anhydrous)

$$Ln_2O_3 + 6\,N_2O_4 = 2\,Ln(NO_3)_3 + 3\,N_2O_3$$

Anhydrous nitrates of the rare earths may be obtained from the oxides by heating with NH_4NO_3 or, better, by treatment with liquid N_2O_4. However, $Nd(NO_3)_3$ can be prepared only from Nd_2O_3 and N_2O_4; heating Nd_2O_3 with NH_4NO_3 yields $Nd(NO_3)_3 \cdot NH_4NO_3$.

The apparatus for the preparation from the oxides and N_2O_4 is shown in Fig. 289. Drying tower *a*, filled with P_2O_5, is connected to storage bottle *e* through a vacuum-type stopcock *b*. A mercury manometer, which serves as a safety valve, is attached at *f*, and a McLeod gage is connected to *g* via a cold trap. The 150-ml. steel bomb *h* is equipped with a needle valve at the top and a square thread screw at the bottom; the latter is for the introduction of the dry oxide (about 2 g.) and removal of the reaction product. The bottom neck of the bomb and the corresponding surface of the screw head have machined seats for a lead O-ring. Lead packing may also be used at the junction of the bomb and the needle valve. The metal and glass tubes are connected at *i* by means of a cement seal (for example, Glyptal). Two stopcocks, *c* and *d*, and a cold trap *k* complete the system.

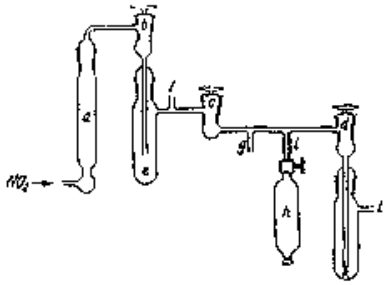

Fig. 289. Preparation of anhydrous rare earth nitrates. *a* drying tower; *b*, *c*, *d* vacuum-type stopcocks; *f*, *g* connections to manometers; *h* steel bomb; *k* cold trap.

The apparatus is evacuated through *l* to about 0.02 mm. Stopcock *c* is closed and about 30 ml. of liquid N_2O_4 is condensed in *e* by cooling with liquid N_2. Then *c* is opened, *b* and *d* are closed, and the N_2O_4 is distilled into the steel bomb *h* (40 °C water bath at *e*, cooling with liquid N_2 at *h*). The needle valve is closed and

the bomb disconnected at *i*. A steel jacket is screwed on and the bomb is heated for 24 hours at 150°C. After cooling, the N_2O_4 is removed (vacuum) via a system of drying towers filled with $Mg(ClO_4)_2$ and collected in a trap cooled with Dry Ice–acetone.

The last traces of N_2O_4 are removed by heating the product in a drying pistol at 137°C (boiling xylene). Very pure nitrates are obtained in 100% yield.

Up to now, this method has been used for the preparation of the nitrates of Y, La, Pr, Nd, Sm and Gd. For the preparation of $(NH_4)_2Ce(NO_3)_6$, see G. F. Smith, V. R. Sullivan and G. Frank, Ind. Eng. Chem., Anal. Edit. 8, 449 (1936), as well as p. 1133 f. of this Handbook.

PROPERTIES:

Loose powders; form clear solutions with water and ethanol (very exothermic process). The nitrate colors differ only slightly from those of the corresponding anhydrous chlorides.

REFERENCE:

T. Moeller and V. D. Aftandilian, J. Amer. Chem. Soc. 76, 5249 (1954); T. Moeller, V. D. Aftandilian and G. W. Cullen in: W. C. Fernelius, Inorg. Syntheses, Vol. V, New York–London, 1957, pp. 37–42; L. F. Audrieth, E. E. Jukkola, R. E. Meints and B. S. Hopkins, J. Amer. Chem. Soc. 53, 1807 (1931).

Rare Earth Cyclopentadienides

$$Ln(C_5H_5)_3$$

$$LnCl_3 + 3\,NaC_5H_5 = Ln(C_5H_5)_3 + 3\,NaCl$$

The anhydrous rare earth chloride, in tetrahydrofuran solution, is treated (stirring) with the stoichiometric quantity of cyclopentadienylsodium. The solvent is then removed by distillation and the product is sublimed at 200–250°C in vacuum (10^{-4} mm.).

Up to now, only the tricyclopentadienides of Sc, Y, La, Ce, Pr, Nd, Sm and Gd have been prepared.

PROPERTIES:

Crystalline compounds; begin to decompose above 400°C. Insoluble in hydrocarbons, soluble in tetrahydrofuran and

1,2-dimethoxyethane. Decompose in water to cyclopentadiene and the hydroxide. Quite stable in air, with the exception of $Co(C_5H_5)_3$.

REFERENCE:

G. Wilkinson and J. M. Birmingham. J. Amer. Chem. Soc. 76, 6210 (1954).

SECTION 22

Titanium, Zirconium, Hafnium, Thorium

P. EHRLICH

Titanium

Ti

Due to its great affinity for a large number of elements, the preparation of titanium poses considerable difficulties. In particular, N, C and O dissolve to an appreciable extent in the metallic phase, and cause cold-shortness even when present in minute quantities. They cannot be removed either chemically or by sintering or melting in high vacuum. Consequently, the relatively easy conversion of TiO_2 with Ca (method I below) yields only 98% pure metal, even under conditions where the highest purity of apparatus and raw materials is maintained.

Pure metal that is ductile while cold can therefore be prepared only by methods which use halides as the starting materials. However, these procedures, which are based on the reactions K_2TiF_6 (or Na_2TiF_6) + Na (method II) or $TiCl_4$ + Na (method III below), suffer from the drawback that the deposited metal is usually porous or flaky, which leads to reoxidation during the removal of the alkali halide by-product; it is therefore used only as a crude starting material for the purification process. Nevertheless, careful adherence to a number of precautionary measures permits the preparation, even by these methods, of pure metal which can be cold-worked. The Kroll magnesium process (method IV), which utilizes the reaction between $TiCl_4$ and Mg, is used at present both in the laboratory and in industry.

The highest purity (0.03% C and ~0.006% N) is attained via the elegant recovery process of van Arkel and de Boer (method V below). This is based on the thermal decomposition of titanium iodide at 1100–1500°C.

I. PREPARATION OF CRUDE METAL FROM THE OXIDE AND CALCIUM

$$\underset{79.9}{TiO_2} + \underset{80.2}{2\,Ca} = \underset{47.9}{Ti} + \underset{112.2}{2\,CaO}$$

When only crude starting metal for the refining process is desired, the preparation may be simplified and carried out in

a bomb made of two steel sections welded together. Section 1 (the one of larger diameter) consists of a tube of type 304L stainless or low-carbon steel with a welded-on bottom. A wall thickness of 1 mm. is sufficient if the tube diameter does not exceed 25 mm. This section is annealed at 1000°C in moist H_2 (for more efficient removal of the P and C present). A second, crucible-like section, 40–60 mm. long, of exactly the same shape and precisely fitting into the first section (in such a way that the two sections telescoped together make up a vessel closed on all sides), is charged with the starting materials and forced as far as possible into the first section in order to reduce the air space inside to the minimum and to give the tightest possible seal between the two walls. If this is done, then the rims of the two tubes may be welded together without a welding rod; the lower section of the tube, that is, the section encompassing the charge, is cooled in water during the welding operation. One can avoid, to a large extent, the penetration of the welding gases into the bomb either by extending the sealing surface between the two tubes (that is, by using longer tubes for an identical charge), or by crimping the upper rim of the outer crucible around the inner one. As an explosion protection, and to provide a backup to strengthen the bomb walls, a closely fitting external tube or jacket, made of the same material and open at both ends, should surround the bomb. Scaling of the bomb may be prevented by preheating the latter inside a porcelain tube in a stream of H_2; if the heating must be carried out in air, a coat of aluminum-bronze paint will prevent too rapid oxidation of the tube.

Following the reaction (see description below) the bomb is allowed to cool completely before being sawed open. The sawing should not introduce any iron filings into the product (avoid tilting the bomb during sawing or cutting at an angle). The reaction product can usually be loosened by gentle tapping with a hammer while the tube is clamped in a vise. Alternatively, the crucible may be sawed open along its length and the steel jacket is just peeled off.

Only Si-free, well-dried TiO_2 starting material should be used, to avoid formation of silicon or silicides. If this precaution is not taken, these impurities are carried over in the subsequent refining process and are incorporated into the titanium ingot. Furthermore, the reduction should be carried out only with distilled Ca; addition of distilled Na is advantageous. Thus, the reduction of 25 g. of TiO_2 with a mixture of 40 g. of Ca and 20 g. of Na yields about 13 g. of crude Ti (with a metal content of about 90%). Heating for 20 minutes at 1000°C suffices for complete reduction. After cooling and opening the tube, the contents are ground to pea size and leached with alcohol, water and increasingly concentrated portions of hydrochloric acid. The residue

is washed free of chloride, the water is removed with alcohol, and the product is dried at 110°C.

The preparation of titanium that is malleable when hot (>200°C) by this process is described by Kroll. Pure TiO_2 (770 g.), turnings of distilled Ca (770 g.), and fused and pulverized $CaCl_2/BaCl_2$ (750 g./250 g.) are mixed and pressed into briquets, which are allowed to react under 99.2% Ar in an electric furnace at > 700°C. The addition of the salts is necessary to moderate the reaction and, above all, to prevent the formation of $CaTiO_3$, a product which does not react with Ca even on repeated reduction. The use of CaH_2 in the second reduction has proved useful, since the powdery hydride mixes very readily with the other reactants while the nascent H_2 it evolves is a powerful reducing agent. Thus, 348 g. of Ti (from the first reduction stage) + 400 g. of $CaCl_2/BaCl_2$ (3:1) + 50 g. of Ca + 50 g. of CaH_2 gave a yield of 337 g. of metal after heating for one hour at 1000°C under 99.6% Ar. The very well-sintered product is crushed and washed with water and concentrated hydrochloric acid, yielding fairly homogeneous granules.

The original reference covers the constructional details of the furnace.

With sufficiently small inputs (20–30 g. of TiO_2) the second reduction may also be carried out in the welded bomb and without the addition of CaH_2; the temperature should then be 1000°C (see also the procedure for Th, method II).

As in the preparation of the rare earth metals [F. H. Spedding et al., Ind. Eng. Chem. 44, 553 (1952)] the addition of free iodine to the reduction mixture is recommended, since the large heat of formation of CaI_2 facilitates fusion of the metal.

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II. PREPARATION OF CRUDE METAL FROM FLUORIDES AND SODIUM

$$\underset{207.9}{Na_2TiF_6} + \underset{92.0}{4\,Na} = \underset{47.9}{Ti} + \underset{252.0}{6\,NaF}$$

or

$$\underset{240.1}{K_2TiF_6} + \underset{92.0}{4\,Na} = \underset{47.9}{Ti} + \underset{116.2}{2\,KF} + \underset{168.0}{4\,NaF}$$

The fluorotitanates are prepared by dissolving pure TiO_2 in an excess of warm 20–40% hydrofluoric acid, treating the mixture with a stoichiometric quantity of NaOH or KOH, evaporating the solution without overheating (at 40–60°C) until saturation, and allowing the product to crystallize. In the case of the potassium salt, the product is the monohydrate; it is readily recrystallized from water. Heating of the air-dried product for two days at 35°C readily yields the anhydride, which in air at 500°C decomposes

to the oxyfluoride. The Na_2TiF_6 crystallizes already as the anhydrous salt and may be obtained in 99.9% purity by repeated precipitation with alcohol from aqueous solution. The small amount of water remaining in the product after drying in air is difficult to remove by heating without causing partial hydrolytic decomposition [H. Ginsberg and G. Holder, Z. anorg. allg. Chem. 190, 407 (1930); 196, 188 (1931); 201, 198 (1931); 204, 225 (1932)].

The Na_2TiF_6, in portions of up to 1 kg., may be readily reduced with a 10% excess of Na in a bomb. The sodium is cut into small cubes and mixed with the hexafluorotitanate. After filling, the bomb is welded as in method I and heated to 1000°C. It is imperative that the fluoride be absolutely dry, otherwise an explosion may occur.

When K_2TiF_6 is used in the same process, a Na excess of only 1% is used, to prevent the formation of too much K, which may cause ignition of the mixture upon opening of the tube.

The one great disadvantage of this process is the fact that removal of the fluorine from the product requires very long boiling with large quantities of water. Direct washing of the fluorine-containing reaction mass with hydrochloric acid is not feasible, since the alkali fluorides react with the acid to form hydrofluoric acid, which dissolves the titanium metal. On the other hand, boiling with water results in considerable oxidation; the Ti thus produced may contain more than 20% of the oxide. After the treatment with water, the metal is boiled a few times with aqueous sodium hydroxide and is then treated with cold, dilute hydrochloric acid (too much Ti goes into solution with warm acid).

III. PREPARATION OF CRUDE METAL FROM CHLORIDE AND SODIUM

$$\underset{189.7}{TiCl_4} + \underset{92.0}{4\,Na} = \underset{47.9}{Ti} + \underset{233.8}{4\,NaCl}$$

If the reagent quantities are small, the welded steel bomb described in method I can be used. The temperatures must be very high (to start the reaction, the bomb must be red-hot) and thus the $TiCl_4$ vapor pressure is very high. Larger quantities (500 g. of $TiCl_4$ + 245 g. of Na) must therefore be heated in a thick-wall steel bomb, the lid of which is sealed on with a copper gasket and secured with a heavy screwed-on cap.

The $TiCl_4$ pressure in the bomb can be kept low by one of two methods: *a*) the starting temperature of the reaction may be lowered by the addition of a tablet of $KClO_3$-Na; the small amount of oxygen introduced is not detrimental provided only crude metal is desired; *b*) the reaction tube may be constructed in such a way that there exists a temperature gradient and only the sodium is heated to 700–800°C.

If the amount of starting material is not too small, the heat of reaction developed in the process is sufficient to cause sintering of the metal; the heat may even be sufficient for partial melting of the charge. The product titanium is first washed with alcohol to remove the excess sodium, then with water to remove salts, and finally with dilute hydrochloric acid. After repeated washing with water, alcohol and ether, the metal is dried in a vacuum desiccator. Assuming the above-mentioned charge of 500 g. of $TiCl_4$, the product consists of about 31.5 g. of half-fused metal and 4.5 g. of fine powder, as well as 71 g. of lumps and grains whose Ti content ranges between 96 and 99.5%. The powder fraction oxidizes quite readily.

This metal is much better suited as crude Ti for the refining process than the product obtained from the hexafluorotitanate.

In the industrial Degussa process, 46 kg. of Na is heated to 700–800°C. Then, 85 kg. of $TiCl_4$ is piped onto a layer of molten KCl/NaCl (15/15 kg.) situated below the Na. The resultant metal consists of 98% Ti and 2% Fe.

IV. KROLL MAGNESIUM PROCESS

$$\underset{189.7}{TiCl_4} + 2\,\underset{48.6}{Mg} = \underset{47.9}{Ti} + 2\,\underset{190.4}{MgCl_2}$$

A) PREPARATION OF THE METAL

Magnesium works just as well in the reduction of $TiCl_4$ as sodium; in addition, commercial magnesium is already very pure and may be handled in air without special precautions. Thus, magnesium is the preferred reducing agent.

The reduction apparatus is shown in Fig. 290.

Since titanium attacks iron at high temperatures, the entire reaction zone of the crucible must be lined with a 1.5-mm.-thick sheet of molybdenum. Although molten Ti also adheres to molybdenum, the two metals can later be separated on a lathe. The $TiCl_4$ itself does not react at high temperatures with either Fe or Mo; the only precaution necessary is to keep all iron parts inside the furnace oxide-free.

The reaction crucible *b*, lined with molybdenum sheet *c*, is charged with 360 g. of very pure Mg blocks (the Mg metal surfaces are precleaned with a file). The adapter cover *e*, which carries the dropping funnel *m* and the Ca electrodes, is put in place and the entire system is evacuated to 0.1 mm. Very pure Ar is introduced, and an electric arc is struck and maintained for 10 min. between the two Ca electrodes *o*; the resultant Ca vapor serves as a scavenger for moisture and impurity gases. Final drying of the Ar is achieved by dropwise addition of a small quantity of $TiCl_4$ from the small dropping funnel *m*.

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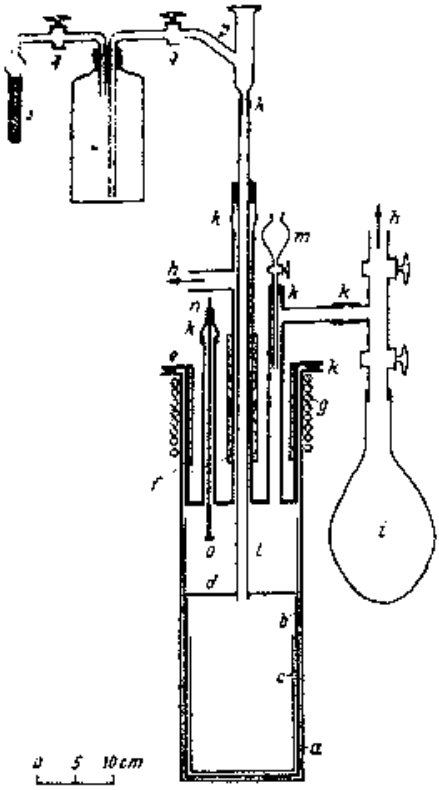

Fig. 290. Preparation of titanium metal from titanium (IV) chloride and magnesium. *a*) chrome-nickel alloy outer container (Inconel, Nichrome, or other similar alloys may be used); *b*) iron crucible; *c*) molybdenum lining; *d*) iron-plate lid; *e*) adapter cover; *f*) cooling chambers; *g*) cooling coils (lead); *h*) vacuum line; *i*) rubber balloon for Ar; *k*) rubber connections and seals; *l*) iron inlet tube for $TiCl_4$; *m*) dropping funnel with $TiCl_4$; *n*) electrodes; *o*) calcium rods; *p*) glass adapter for a sight glass; *q*) stopcocks; *r*) storage bottle with $TiCl_4$; *s*) $CaCl_2$ tube.

When the alloy container *g* reaches a temperature of about 700°C, 500 ml. of $TiCl_4$ is slowly added to the reaction chamber from the storage bottle *r*. The addition rate is such that it takes 1.5 hours to add all of the $TiCl_4$. The temperature, which rises to about 1050°C, should be precisely controlled during the entire addition. The remaining 150 ml. of $TiCl_4$ is then added very slowly over a period of 0.5 hour, the temperature being gradually raised above the boiling point of Mg (to a maximum of 1180°C).

The molten Mg creeps over the surface of the nascent clumps of Ti, thus constantly contacting fresh $TiCl_4$. In the process small quantities of Mg and $MgCl_2$ are occluded in the Ti; the final heating of the iron crucible to above the boiling point of Mg is intended to counteract this phenomenon.

The progress of the reaction may be observed through the quartz window set in adapter *p*. If the rate of addition of $TiCl_4$ is not precisely controlled, the inlet tube *l* may become plugged with Ti sponge.

After cooling in argon, the crucible is full of large clumps of light Ti metal embedded in white $MgCl_2$ crystals. The metal contains extremely finely divided Mg and $MgCl_2$; however, no Mg–Ti alloy is formed. This mass is removed from the crucible with the help of a lathe, cutting as far as the molybdenum lining; the pieces of Ti are held so firmly in the surrounding $MgCl_2$ that metal turnings can be produced without any difficulty. These are first very carefully leached with water, and are then treated with an excess of dilute HCl. Decantation yields about 1% of the product in colloidal form. The smaller turnings are wet-ground in a ball mill and worked up separately. They are unsuitable for the production of ductile Ti. The coarser pieces are crushed to 10–12 U. S. mesh size, and this coarse metal powder is rewashed, separated from the fines, and etched with hot hydrochloric acid (1:3) until the acid becomes deep violet. The acid treatment is necessary because the crushing operation oxidizes the surface of the metal particles (in contrast to the zirconium oxides, the titanium oxides can be removed by acid leaching). After another washing procedure, first in cold 5% hydrochloric acid and then in water, followed by drying, the powder is freed of Fe with a magnet, rescreened, washed with alcohol and dried at 120°C. The yield of Ti metal is 284 g. (95.9%).

Worner, as well as Wartmen et al., has modified the above procedure in several respects. They carry out the reaction in vacuum; however, this necessitates the use of a double-walled container. The addition of $TiCl_4$ is carried out much more rapidly (80% at 30–40 ml./min., the remainder at 10 ml./min.), so that 1500°C temperatures occur locally, and external heating may be stopped as early as five minutes after the start of the $TiCl_4$ addition. When the reaction is complete, heating at 900°C is continued for 45 minutes. The reaction product is not leached; $MgCl_2$ and unreacted Mg are partly removed by evaporation and partly by fusing and draining.

B) REMELTING OR RESINTERING OF THE METAL

The Ti sponge may be converted to solid metal by fusion in an arc furnace, in which either high vacuum or a pure argon (99.92%) atmosphere is employed; the other acceptable procedure is sintering with alternating pressing and heating in high vacuum (10^{-4} mm.) at 1000°C. The Ti powder may also be hot-rolled in air while contained in a welded steel container. In the last case, contamination with Fe is slight and the iron is easily removed by etching the ingot after unwinding the steel sheet. For further details, see the original references.

Assuming that the proper conditions are observed, the product metal is about 99.8% pure, and contains 0.06% Fe, 0.1% O, 0.02% N and 0.02% $MgCl_2$.

V. THE REFINING PROCESS OF VAN ARKEL AND DE BOER

$$TiI_4 = Ti + 2I_2$$
$$555.6 \quad 47.9 \quad 507.7$$

a) The iodides are used for the preparation of small quantities (~20–30 g.) of metal; these highly hygroscopic compounds are not introduced directly as raw materials, but are produced as intermediates during the process in which they form from crude metal and iodine. The most suitable crude titanium for this process is that prepared from $TiCl_4$ and Na. Titanium oxide, nitride or carbide are attacked by the iodine; thus, the corresponding nonmetals are left unchanged and do not incorporate into the growing metal ingot. The weak point of this refining process is that a considerable number of other metals (e.g., Zr, Hf, Th, V, B, Si, as well as Al and Fe if the filament temperature is low) are codeposited with the desired titanium; therefore, these impurities should be removed during the preparation of the crude metal, that is, prior to refining.

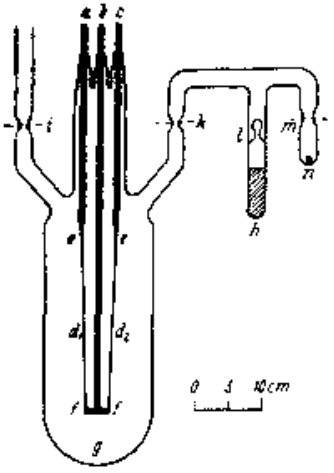

Fig. 291. Preparation of titanium metal by the process of van Arkel and de Boer. *g*) pyrex bulb; *a*, *b*, *c*) triangular arrangement of tungsten bus bars; d_1, d_2) tungsten wires; *h*) iodine storage flask; *l*) shatter valve; *n*) steel ball.

The Pyrex thermal decomposition flask is shown in Fig. 291. The tungsten bus bars *a*, *b* and *c* (diameter of each 6 mm.) are arranged in a triangular pattern and sealed into the glass. The Ti deposits on drawn tungsten core wires (d_1 and d_2), each 0.04 mm. thick and 400 mm. long.

These wires cannot just simply be stretched directly between the electrodes, as would appear from the drawing. If this were done, the rapid rate of heat conduction through the tungsten rods could cause excessive cooling of the wire ends and consequently prevent the titanium from depositing at the cold spots. This would result in nonuniform deposition, that is, preferential accumulation of the metal on the glowing sections, which would thus become heavier and unbalance the entire wire. Consequently, after a certain time has elapsed, the slightest mechanical shock would be sufficient to break the thin wires and interrupt electrical

contact. The critical spots *e* and *f* should therefore be strengthened by insertion of reducer pieces made of progressively thinner tungsten wires. The simplest arrangement consists of a 1-mm.-thick wire ring fixed in a slit in the bus bar; this ring, in turn, is fitted with a drilled 0.2-mm. ring to which the glowing wire is attached.

Crude Ti (40 g.) is placed in *g* and 12 g. of I_2 in evacuated space *h*. The flask is evacuated to $<10^{-3}$ mm. and the metal is degassed by heating to about 500°C. At the same time, the entire glass part of the apparatus (except for the iodine tube) is dried and degassed by fanning with a flame while the reduced pressure is maintained. As soon as a sufficiently high vacuum has been restored, a predetermined starting current (about 0.25 amp.) is applied to the tungsten wires to bring them to a "black body temperature" of 1400°C, as measured by an optical pyrometer. The system is cooled and sealed at *i*, the thin glass partition *l* is broken by means of an electromagnet and steel ball *n*, and the I_2 from *h* is allowed to flow into *g*. A temperature of 200°C is sufficient for a rapid reaction of the iodine with a portion of the Ti, a reaction sometimes even accompanied by the appearance of a flame. Following this the apparatus is melt-sealed at *k* and heated to 550°C in a furnace; the tungsten wire d_1 is then brought to a glow at the same current as above. The apparent temperature read on the pyrometer is now lower because of the colored vapors rising from the material. This temperature must be held constant during the entire subsequent procedure (by increasing the current as the thickness of the deposited Ti layer increases).

The equilibria prevailing in the system are highly temperature-dependent. Furnace temperatures below 250°C produce TiI_4, which then decomposes on the hot wire in accordance with the above equation. At higher temperatures, TiI_4 reacts with the crude Ti to form TiI_2, which has a considerably lower vapor pressure. Only at temperatures above 500°C does this pressure become large enough to again produce titanium deposition on the glowing wire. The Ti metal formed at higher temperatures is so free of iron that the latter cannot even be detected.

Gases which may still be present in the flask during the refining of the Ti are bound by the metal (thus, a small amount of nitride is often formed). For this reason, the current to the first wire is shut off after a certain time and that to the second wire, d_2, is turned on; the Ti metal which then deposits on d_2 is completely pure. Because of the gradual build-up of titanium, the current must be raised up to 200 amp. when the ingot reaches a thickness of about 5 mm. This requires about 24 hours; if the starting material is the crude Ti obtained from the hexafluorotitanate, the build-up rate is lower.

The current to the furnace can be gradually reduced to zero in the course of the run, since the growing Ti rod begins to radiate

enough heat to maintain the required temperature throughout the system (toward the end of the run, it may even be necessary to cool the furnace space with air).

If the crude metal used in the refining process is prepared from pure starting materials, the resultant smooth Ti rod is almost completely pure, since the tungsten wire substratum constitutes only about 0.01% of the rod. The metal has about the same ductility as Cu, and may therefore be cold-worked and rolled.

The following method is well suited for the conversion of a piece of ductile titanium (it applies also to Zr or Hf) to powder: Ti is treated at 600°C in a stream of H_2. The gas must be extremely pure (see p. 111 ff.). The resultant hydride is brittle and easily ground to a powder. The H_2 may then be removed by heating in high vacuum at 1000°C.

b) This method has recently been used in the U.S. to prepare 700-g. quantities of Ti. The operation is carried out in Pyrex containers 900 mm. long and 200 mm. in diameter, but metal tubes have also been used with great success. For a given size of tube, the metal tubes are much easier to handle and simpler to cool. They contribute to the safety of the operation since an oil bath can then be used. The crude Ti is not placed at the bottom of the tubular vessel but is held in a layer 10–15 mm. thick at the walls by means of a cylinder of perforated Mo sheet. With this arrangement, it is also possible to dispense with the additional furnace heating. The glowing wires, in the form of hairpins, are hung from three tungsten rods; if one wire burns out, two more are still available. Titanium prepared in this manner contains 0.03% C, 0.003% N, 0.002% O, 0.04% Si, 0.04% Fe, 0.05% Al and 0.002% S.

VI. PREPARATION BY ELECTROLYSIS OF MELTS

Because of its high melting point, the Ti formed by electrolysis deposits on the cathode in the form of a solid cluster impregnated with the melt. The presence of even minute traces of moisture or oxygen causes the deposition of a finely crystalline material with a high salt content; suitable operating techniques, however, make it possible to obtain large crystals of pure metal.

a) Crude titanium may be obtained by electrolysis of a solution of TiO or mixed TiO–TiC crystals in a $CaCl_2$ melt at 700–850°C.

b) The electrolytic decomposition of K_2TiF_6 in a bath of NaCl, on the other hand, yields a very pure, coarsely crystalline metal. In this process the melt becomes enriched in NaF, according to the overall equation

$$K_2TiF_6 + 4\,NaCl = 2\,KF + 4\,NaF + Ti + 2\,Cl_2$$

while chlorine is evolved on the anode.

c) Another process uses an electrolysis cell in which the cathode chamber is separated from the anode by a diaphragm of sintered alumina; $TiCl_4$ vapor is introduced into a melt of alkali metal chloride or alkaline earth chloride in the cathode chamber. The resultant dissolved lower chlorotitanates decompose to the metal at a later stage of the electrolysis.

d) Metal of very high purity may be recovered from crude titanium or titanium waste by anodic solution of the starting material in a melt of alkali metal chloride containing a small amount of lower titanium chlorides, and reprecipitation of the Ti at the cathode.

VII. REDUCTION OF TiO_2 WITH CaH_2

A mixture of TiO_2 and CaH_2 (in 40% excess) is heated for one hour in hydrogen at atmospheric pressure (electric furnace, 950-1075°C); the product is treated with dilute hydrochloric acid. A fine powder, with a metal content of 96%, is obtained; the remainder is mainly H_2 (3%). This process is also suitable for preparation of V, Nb and Ta from their oxides.

PROPERTIES:

Silvery white, ductile metal. M.p. 1730°C; d 4.45. Crystal type A3. Hexagonal α-Ti converts at 885°C to the body-centered cubic form (β-Ti). Electrical resistivity $\rho = 42 \cdot 10^{-6}\ \Omega \cdot cm$.

Scarcely or not at all attacked by acids and bases; dissolves readily in hydrofluoric acid.

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Zirconium, Hafnium

Zr, Hf

The general remarks concerning titanium apply equally well to zirconium and hafnium. These elements are thus prepared via the same methods and generally in the same equipment as described in detail in the section on titanium. In the following, we shall discuss only those details that differ from the above. Where Hf is not discussed separately, the conditions specified for Zr apply.

I. $$\underset{123.2}{ZrO_2} + \underset{80.2}{2\,Ca} = \underset{91.2}{Zr} + \underset{112.2}{2\,CaO}$$

Crude starting Zr for the refining process is prepared via the sealed bomb method, with corresponding changes in the amounts of materials used, chiefly the addition of Na, which is

highly recommended for the reduction of ZrO_2 (e.g., 20 g. of ZrO_2 + 20 g. of Ca + 10 g. of Na); heating to 1300°C produces a metal still containing oxygen. Although this causes cold-shortness, the metal becomes malleable somewhat above 200°C.

II. $$\underset{283.4}{K_2ZrF_6} + \underset{92.0}{4\,Na} = \underset{91.2}{Zr} + \underset{116.2}{2\,KF} + \underset{168.0}{4\,NaF}$$

Crystalline K_2ZrF_6 (60 g.), prepared by cooling a heated solution of the hydroxide in KHF_2, is heated with 27.5 g. of Na in a sealed bomb at 1200–1300°C. The resultant 18 g. of crude metal is a suitable material for the refining process.

III. $$\underset{233.0}{ZrCl_4} + \underset{92.0}{4\,Na} = \underset{91.2}{Zr} + \underset{233.8}{4\,NaCl}$$

Up to 1 kg. of sublimed $ZrCl_4$, crushed to lumps, and 450 g. of distilled Na may be reacted in one run in a sealed steel tube at 850°C. The bottom of the tube is charged with a layer of Na; this is followed by the reaction mixture ($ZrCl_4$ + Na), topped with a layer of Na. Since the vapor pressure of $ZrCl_4$ is considerably lower than that of $TiCl_4$, the processing of larger quantities is simpler. The heat evolved in the reaction is so large that partial sintering of the metal occurs.

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IV. $$\underset{233.0}{ZrCl_4} + \underset{48.6}{2\,Mg} = \underset{91.2}{Zr} + \underset{190.4}{2\,MgCl_2}$$

As in the magnesium process for Ti, Zr may be prepared by reduction of $ZrCl_4$ vapor with Mg in a helium atmosphere (see references below for further details).

V. $$\underset{598.9}{ZrI_4} = \underset{91.2}{Zr} + \underset{507.7}{2I_2}$$

The glowing wire temperatures during refining should be ~1400°C in the case of Zr and ~1600°C in the case of Hf. The Pyrex vessel must be kept at 600°C. The crude metal obtained from the chloride is the most suitable raw material. Recently Zr has been prepared in large glass vessels in the form of rods weighing up to 200 g.

PROPERTIES:

Silvery white, ductile metals.

	Formula weight	M.p.	d	α (close-packed hexag.) → β (bcc.)	Resistivity
Zr	91.22	1860°C	6.50	870°C	$41 \cdot 10^{-6}$ Ω · cm
Hf	178.6	2230°C	13.3	~1500°C	$30 \cdot 10^{-6}$ Ω · cm

Scarcely or not at all attacked by acids and bases; dissolve readily in hydrofluoric acid. For the pulverization of solid metals via hydrogenation and dehydrogenation (hydrides), see pp. 1170 and 1184.

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Thorium

Th

Despite the close resemblance in chemical behavior of the metals and their compounds, thorium differs from titanium, zirconium and hafnium in one respect, and that makes the preparation of

the metal much easier. Thus, although the affinity of thorium metal for O, N and C is large, its cubic face-centered lattice cannot accommodate these nonmetals in solid solutions. The result is that, even on incomplete purification, these nonmetals are present only in the form of compounds and in small quantities; they have thus little effect on, for example, the mechanical properties of the metal. For this reason Th may be obtained in a cold-workable form by pressing and sintering the powder.

In contrast to titanium and zirconium, the preparation of thorium metal via reduction of the oxide with calcium (method II) acquires increased importance and rivals the reduction of the tetrachloride with sodium (method I). Melt electrolysis (method III) is another possibility. Neglecting the small oxide content (up to 1%), which in any case has never been determined precisely, the metal obtained by any of the three methods is already quite pure and contains only 0.1–0.2% of other impurities. The Th prepared by the refining process (method IV), is definitely oxygen-free and should in any case yield the purest product.

I. REDUCTION OF THE TETRACHLORIDE WITH SODIUM

$$\underset{379.9}{ThCl_4} + \underset{92.0}{4\,Na} = \underset{232.1}{Th} + \underset{233.8}{4\,NaCl}$$

Up to 300 g. of oxychloride-free sublimed $ThCl_4$ may be reacted at 500°C with vacuum-distilled Na (25% excess) in a welded iron bomb (see method I, section on titanium). The iron crucible should be filled with the reaction mixture in the same way as in the reaction between $ZrCl_4$ and Na, that is, layer by layer. Following the reaction, the bomb is completely cooled, opened and the reaction product treated, first with alcohol (to remove the excess Na), then with water (always maintaining the solution on the alkaline side). After complete removal of the chlorine, the residue is treated with 2N HNO_3 to dissolve any $Th(OH)_4$ which may be present, filtered with suction, thoroughly washed with water, alcohol and ether, and dried in vacuum at 300°C. The metal yield is 55%, in the form of lead-gray platelets and pellets. The coarsest particles are also the purest and contain 0.1% O (1% ThO_2).

II. REDUCTION OF THE OXIDE WITH CALCIUM

$$\underset{264.1}{ThO_2} + \underset{80.2}{2\,Ca} = \underset{232.1}{Th} + \underset{112.2}{2\,CaO}$$

A) PREPARATIVE PROCESS

The process is based on the reduction of very pure ThO_2 with distilled Ca in the presence of anhydrous $CaCl_2$ heated to 450°C.

The $CaCl_2$ melts at the temperature of the reaction, affording a liquid reaction medium. The heavy Th product settles to the bottom and is thus protected by a layer of melt. The apparatus is either a steel bomb capped with a threaded conical lid (cf. the paper of Marden and Rentschler) or the simpler welded steel tube described under method I for the preparation of Ti. The charge, which is made up of four parts of ThO_2, four parts of $CaCl_2$ and three parts of ground Ca, is vigorously shaken in a closed bottle to achieve the most complete mixing possible. The bomb is filled rapidly, sealed and heated for one hour at 950°C. The tube is then cooled and opened; the resultant pea-sized reaction product is gradually added to water (about two liters per 40 g. of starting ThO_2) with vigorous stirring to prevent a local temperature rise. After the calcium has completely reacted with the water and the evolution of gas ceases, stirring is stopped, the supernatant liquid is decanted, and the solid is washed four times with two-liter portions of water, vigorously shaking each time for 5-10 minutes. The decanted supernatants are low-concentration suspensions of dark, fine Th. Finally, 200 ml. of water is added to the remaining heavy residue, followed by 25 ml. of conc. nitric acid (vigorous stirring). The odor of acetylene is noticeable, and if the ThO_2 used in the preparation was made from thorium nitrate which contained some sulfate, the odor of H_2S will also be present. After 10 minutes, the solution is diluted tenfold, the product is allowed to settle, the supernatant is decanted, and the acid treatment is repeated once or twice. After thorough washing with water (twice, two liters each time), the product is suction-filtered, treated with alcohol and ether, and dried in vacuum at 300°C. Under favorable conditions, the relatively coarse, dark gray powder is obtained in 90% yield.

Kroll uses the same process with a suitable salt melt. However, instead of working in a sealed bomb, he uses an iron crucible placed in an argon atmosphere.

B) MELTING OF Th POWDER

Small, relatively compact cylinders are formed from thorium powder under a pressure of 6-7 tons/cm^2. Crucibles of sintered thoria are suitable melt containers. The cylinder, wrapped in a tungsten wire spiral, is placed inside such a crucible which is set up in a quartz container connected to a high-vacuum pump. The material is heated with a high-frequency induction coil.

The apparatus is evacuated and the sample carefully degassed by slow heating while the vacuum is maintained. With coarse metal powder, this operation requires about half an hour, and longer with fine powders; the reaction is essentially complete when the powder reaches red heat. The temperature is then rapidly

increased to melt the metal. Oxidation is prevented if air is excluded from the system until after complete cooling.

Thorium powder with a completely clean surface is noteworthy for its sensitivity to air after high-vacuum degassing at 400°C. This sensitivity is so pronounced that the metal catches fire on coming in contact with air. The material also reacts so vigorously with H_2 that it becomes red hot.

III. ELECTROLYSIS

$$\underset{552.2}{Th(NO_3)_4 \cdot 4\,H_2O} \rightarrow \underset{368.2}{KThF_5} \rightarrow \underset{232.1}{Th}$$

The electrolysis of a solution of $KThF_5$ in a NaCl–KCl melt yields very pure metal, containing only 0.02% C, 0.05% Si, 0.005% Fe and a negligible amount of other impurities.

The $KThF_5$ is prepared by dissolving 400 g. of $Th(NO_3)_4 \cdot 4\,H_2O$ in two liters of water and adding, with constant stirring, a solution of 250 g. of KF in 400 ml. of water. The $KThF_5$ precipitate is allowed to settle, washed by decantation until the washings are free of nitrate, suction-filtered and dried for several hours at 125°C.

A cylindrical graphite crucible serves both as the electrolysis vessel and as anode. The inside diameter is 6 cm. and the height 15 cm., with a wall thickness of 1–2 cm. Current is supplied through a strip of Ni sheet wrapped around the upper part of the outside wall. The cathode is a strip of Mo sheet 0.05 mm. thick and 1 cm. wide, which reaches 2.5 cm. from the bottom. The graphite cell stands in a suitable refractory container wound with the heating filament. The entire apparatus is placed inside a sheet-metal vessel filled with thermal insulation (see also the similar arrangement described for the electrolysis of uranium).

A mixture of 250 g. each of KCl and NaCl is melted, and 30 g. of $KThF_5$ is added. When the melt is homogeneous, electrolysis proceeds, with the above Mo cathode, at a temperature of 775°C. A current of 18–20 amp. is required if the submerged cathode surface area is about 20 cm^2. After 20 minutes the cathode is carefully removed from the liquid and replaced with a new piece of Mo, 30 g. of $KThF_5$ is added, and the electrolysis is continued for 20 minutes more. This procedure may be repeated several times.

For preparations on a somewhat larger scale, a larger crucible, capable of containing about 1 kg. of the melt, and a molybdenum cathode 2.5 cm. wide are used. The procedure is the same, except that the $KThF_5$ additions are increased to 60 g., the current to 45 amp., and the cathode area to 50 cm^2. Eightfold repetition of the operation in this larger equipment permits the preparation of about 130–140 g. of Th (58% yield).

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The material adhering to the cathode strip is a mixture of metallic Th and solidified melt. After complete cooling, the salt and the finely powdered, readily oxidized metal fraction are removed by treatment with water. The residual coarse-grained Th is treated three times with nitric acid (1:10) and washed with water. This metal powder is then suction-filtered, washed with alcohol and ether, and dried in vacuum at 300°C.

IV. REFINING PROCESS

$$\underset{739.8}{ThI_4} = \underset{232.1}{Th} + \underset{507.7}{2I_2}$$

The thorium metal prepared by the above process is very pure and absolutely free of oxygen. The procedure is essentially the same as that described for Ti, except that the temperature of the glowing wire is higher (1700°C). The starting material may be any kind of crude thorium, provided it is free of metals which will also deposit on the glowing wire; the product derived from the chloride is very suitable.

PROPERTIES:

Gray powder, solid similar to platinum. Relatively soft and ductile; these properties are unaffected by the presence of small quantities of oxide. M.p. 1830°C; d 11.7. Crystal structure: type A 1.

Hardly or not at all attacked by dilute acids (including hydrofluoric); dissolves readily in fuming hydrochloric acid and especially in aqua regia. Resistant to strong bases.

Thorium powder may be prepared from the solid via the hydride. The procedure is identical to that described on p. 1170 for Ti and Zr; the hydride should be decomposed above 700°C.

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Separation of Zirconium and Hafnium

Hafnium does not occur as a separate mineral, but appears in nature as the always present companion of Zr; the Hf/Zr weight ratio is usually in the range of 0.01-0.025. The preparation of Hf or the purification of Zr thus always involves the isolation of Hf from the crude chlorination product or from commercial Zr compounds. The following fractionation processes are of practical importance:

I. Crystallization
II. Precipitation
III. Distillation
IV. Ion exchange and adsorption
V. Partition between two solvents

I. CRYSTALLIZATION

This method, which is unwieldy and applicable only to the separation of very small quantities of material, has been abandoned for all practical purposes.

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II. PRECIPITATION

Good separation is obtained by precipitation of the phosphates; the hafnium concentrates in the less soluble fractions. A detailed description of the recovery of Hf from cyrtolite, a silicate of very high Hf content (5.5% HfO_2), is given in E. M. Larsen, W. C. Fernelius and L. L. Quill in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 67.

III. DISTILLATION

Since the vapor pressures of $ZrCl_4$ and $HfCl_4$ are virtually the same, the process makes use of their adducts with PCl_5 or $POCl_3$. When a 50-plate glass column is used, the more volatile Hf compound concentrates in the first distillation fraction (5% of the total; 2.5% to 16% HfO_2); the residue remaining after distillation of 40% of the total feed contains only 0.2% HfO_2.

This process seems to have recently assumed a greater industrial importance.

IV. ION EXCHANGE AND ADSORPTION

This process, which was introduced in 1948 by Street and Seaborg for the separation of milligram quantities of Hf and Zr,

becomes important in preparative work only when the small Hf fraction, and not the predominant Zr, may be retained on the column. This is achieved by selective elution of the Zr with 1N H_2SO_4 (which involves the formation of an anionic complex) from a column of synthetic cation exchange resin (method *a*) or by selective adsorption of Hf on silica gel from an anhydrous methanolic solution of the tetrachlorides (method *b*). Although the latter process permits larger throughputs and shorter residence times, work with anhydrous methanol involves difficulties, and the further treatment of the eluate is more troublesome. Method *b* becomes applicable chiefly in those cases when one is forced to deal with tetrachlorides, for example, when the latter are precipitated by chlorination of minerals.

a) Dowex 50 or Zeocarb 225 (350 g., with a particle size of 0.5 mm.) is treated with water for several days and then placed in a tube 120 cm. long and 2.5 cm. in diameter. A solution of 20 g. of $ZrO(NO_3)_2 \cdot 2H_2O$ in one liter of 2N HNO_3 is passed very slowly through the column. (If the nitrate is not available, 24 g. of $ZrOCl_2 \cdot 8H_2O$ is precipitated as the hydroxide, washed thoroughly, and dissolved in one liter of 2N HNO_3.) The material absorbed on the column is eluted with 1N H_2SO_4 (flow rate of 100 ml./hr.). The Hf concentrate begins to appear when 95–98% of the Zr has been recovered (passage of about nine liters of the acid); the HfO_2 content in the Zr salt eluted prior to this point is less than 0.01%.

[For faster throughput rates, one can use the "breakthrough method," in which the initial adsorption on the resin is omitted; the resultant separation is, however, poorer. One proceeds as follows: a solution of 2.5 g. of $ZrO(NO_3)_2 \cdot 2H_2O$ per liter of 1N H_2SO_4 is passed through the above column at a rate of about 200 ml./hr. Before the "breakthrough point" is reached (after the passage of about nine liters), the solution leaving the column contains mainly Zr and a small amount of Hf, whose concentration in the Zr slowly increases to 0.1%. If only seven liters is collected, the product recovered from the solution consists, for example, of 8.2 g. of oxide containing 0.047% of HfO_2.]

After removal of the Zr, the Hf adsorbed on the column is eluted with stronger sulfuric acid (>1.2N); a solution of 0.05 moles of oxalic acid in one liter of 2N H_2SO_4 is an especially good eluent. Thus 63 mg. of Zr-free HfO_2 may be obtained in a 30-g. column, starting from 70 mg. of HfO_2 containing 8% ZrO_2; the material is passed through the ion-exchange column in the form of a solution of $HfOCl_2 \cdot 8H_2O$ in 675 ml. of 1N H_2SO_4.

b) Silica gel (1000 g.) with a specific area of 720 $m.^2/g.$ is purified by treatment with nitric acid (1:1) and washing with water, activated by heating for four hours at 300°C, and suspended in dry methanol; this suspension is placed in a tube 120 cm. long

and 5.0 cm. in diameter. The column then contains about 700 ml. of methanol.

Zirconium tetrachloride (400 g., equivalent to 210 g. of ZrO_2), with a Hf/Zr weight ratio of approximately 0.02, is dissolved in two liters of anhydrous methanol; the solution is allowed to stand for three hours and is then filtered. The filtrate advances through the column at an average rate of 20 cm./hr. (400 ml./hr.).

[The highest separation is achieved during the initial stages, as the following data illustrate:

Cumulative throughput, in g. ZrO_2/g. silica gel	0.05	0.1	0.2	0.25
% Hf in Zr leaving the column	0.05	0.1	0.35	0.6

Thus, one can collect an eluate containing 140 g. of ZrO_2 (equivalent to 265 g. of $ZrCl_4$) with a total Hf concentration of less than 0.1%.

Oddly, much better results are obtained when the operation is conducted on a larger scale. Thus a column 10 cm. in diameter and 150 cm. long charged with 8 kg. of silica gel yields, at correspondingly higher throughputs but otherwise unchanged operating conditions, 1.6 kg. of Hf-free $ZrCl_4$.]

At the point when only about 200 g. of $ZrCl_4$ (equivalent to 100 g. of total oxide) remains in the column, the HfO_2 concentration in this residue becomes 10%. Further concentration is attained by elution of the column with a solution of 2.5 moles of HCl/liter of methanol (preferential desorption of the $ZrCl_4$). Depending on the duration of this treatment, the final elution with 7N H_2SO_4 yields, for example, 60% of the absorbed Hf as a 30% product, or 20% of the metal as a 60% product. These concentrates constitute a very suitable starting material for the extraction process described below.

The silica gel may be reused after reactivation.

V. PARTITION BETWEEN TWO SOLVENTS

The process is based on the preferential ether extraction of Hf from aqueous thiocyanate-containing solutions of Zr and Hf. Addition of acids or salts alters the equilibrium. Thus the presence of ether-insoluble sulfate ions shifts the distribution of Zr and Hf in favor of the aqueous phase, while the addition of acid or NH_4SCN achieves the opposite effect. Since no separation can be achieved by a single-stage extraction, a multistage process must be used. The process is designed to achieve maximum separation by combining the above factors, i.e., by varying the additives in the initial and final stages. Hydrolytic reactions have also been used to advantage in this separation. The following procedure has proven effective for the processing of a raw material containing ~20% HfO_2.

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The ether phase, which is 1N in HSCN, is prepared by shaking one liter of ether with an acidified solution of NH_4SCN (90 g. of NH_4SCN + 1/2 mole of H_2SO_4); the sulfuric acid is added in small portions during the shaking. A mixed oxide $Zr(Hf)O_3$, calcined at not too high a temperature, yields on evaporation with conc. H_2SO_4 a product of the approximate composition $1\ ZrO_2{:}2\ SO_3$. This product, in a concentration of 40-50 g. of oxide/liter of H_2O, is used as the starting material.

One liter of this freshly prepared solution (do not heat to dissolve) is treated with 600 g. of NH_4SCN and vigorously shaken for one minute with one liter of the above ether preparation. After standing for five minutes, the ether layer is siphoned off and transferred to the next stages of the process, where it is treated with solutions of the following composition:

Stage No.	2	3	4	...
$(NH_4)_2SO_4$ (g.)	80	80	80	...
$(NH_4)SCN$ (g.)	50	25	0	...
H_2O (ml.)	500	500	500	...

The initial extraction is repeated ten times, each time with a new batch of the ether-HSCN phase. Each of the resultant ether extracts (fractions 2-10) is then passed through all the successive stages of the process. The aqueous solutions in each stage are, of course, used over and over again; that is, the new ether fraction is treated with the thiocyanate solution remaining in that stage from the extraction of the previous ether fraction. However, it is recommended that the NH_4SCN concentration in the aqueous solutions of stages 2 and 3 be gradually increased (always retaining the thiocyanate gradient shown in the table) and that thiocyanate be gradually added to the succeeding stages. The solution of the last stage must, however, always consist of 80 g. of $(NH_4)_2SO_4$ in 500 ml. of water, so that the ether leaving the system is always washed free of Zr and Hf. Thus, new last stages must be continually added to the series. When the thiocyanate concentration in the aqueous solution of stage 2 reaches twice the level shown in the table, this solution is "retired"; the solution from stage 3 becomes that of stage 2, the solution from stage 4 is shifted to stage 3, and so on down the line. A new thiocyanate-free aqueous stage is then added at the end of the series.

The Hf + Zr concentration and the Hf/Zr ratio must constantly be checked in each stage, since the separation depends on a large number of interdependent factors. Thus, the temperature greatly affects the partition coefficients, an effect which can be compensated for by changes in the volumetric ratios between the phases or by addition of salts.

Some hydrolysis may occur in stage 1; it is recognizable by the appearance of heavy turbidity or precipitation in the aqueous layer, and may necessitate an intermediate treatment (precipitation with ammonia, followed by solution of the precipitate with H_2SO_4).

As has been emphasized before, the process is particularly effective with partially concentrated hafnium products, as shown by the following data. Starting from 40 g. of a product with a HfO_2 concentration of 18%, the aqueous layers of the various stages, after shaking with 10 liters of ether, contained the following proportions of HfO_2:

	1	2	3	4	5	6
Oxide (g.)	28	~4	~5	2	0.6	0.2
HfO_2 (%)	~7	~20	>45	>40	>50	>70

The corresponding figures obtained from a starting material containing 50% HfO_2 were:

HfO_2 (%)	25	~50	~80	~99	>99

Alternate methods: *a*) U.S. authors have used processes involving fractional extraction of the aqueous phase with benzene solutions of diketones [thenoyl trifluoracetone: E. H. Huffman and L. J. Beaufait, J. Amer. Chem. Soc. 71, 3179 (1949); trifluoroacetylacetone: B. G. Schultz and E. M. Larsen, J. Amer. Chem. Soc. 72, 3610 (1950)]. One disadvantage of the thenoyl trifluoroacetone process may be that the Zr, which is usually the major component, is preferentially extracted into the benzene phase.

b) A process in which aqueous solutions of the chlorides are countercurrently extracted with methyl isobutyl ketone in the presence of thiocyanates and thiocyanic acid has attained industrial importance [W. Fischer, H. Heitsch and G. Otto, German Patent 1,010,061, Oct. 18, 1955; Nuclear Sci. Abstr. 10, 371 (1956)].

c) The nitrates of Zr and Hf can be selectively partitioned between aqueous nitric acid and organic solvents, particularly tributyl phosphate and ketones, the Zr being preferentially extracted into the organic phase [R. P. Cox, H. C. Peterson and G. H. Beyer, Ind. Eng. Chem. 50, 141 (1958); Chemie f. Labor und Betrieb, August 1958, 340; W. Fischer and H. Heitsch, German Patent 1,007,306, Nov. 16, 1954; F. Hudswell and J. M. Hutcheon, Proc. Internat. Confer. Peaceful Uses of Atomic Energy, Vol. 8, 563, New York, 1956; J. Huré and R. Saint-James, ibid., 551.]

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Titanium, Zirconium and Thorium Hydrides

Ti/H

Hydrogen dissolves in the Ti metal lattice until a composition $TiH_{0.6}$ is reached; this produces a hydride with a considerable homogeneity in the range of TiH-TiH_2. The upper hydrogen concentration is attainable only with Ti and H_2 of the highest purity, while operating under conditions of extreme cleanliness.

The metal form best suited for the hydrogenation is Ti sponge. Titanium sheet starts to absorb H_2 at 300°C and does so rapidly beginning at 400°C. Partially hydrogenated Ti reacts with carefully purified H_2 even at 20°C. Hydrogen is released from highly hydrogenated products by reheating to above 400°C in high vacuum; complete desorption is achieved at 1000°C.

When it is required to absorb only a predetermined quantity of H_2, the following procedure may be employed. The metal is weighed into a boat of sintered clay (or, better, of stainless steel, provided traces of Fe in the product are not detrimental) placed in a quartz tube connected to the system with a ground joint. The apparatus consists of a glass burette with 0.1-ml. divisions provided with a leveling tube and Hg reservoir and connected to an electrolytic H_2 generator; this apparatus is attached to a high-vacuum system. The quartz tube volume is measured, and the metal is degassed by heating to 550°C. Hydrides with the desired H_2 content are obtained by varying the absorption temperature and the quantity of hydrogen introduced.

Zr/H, Th/H

The preparation of Zr and Th hydrides is similar to the above procedure. Zirconium reacts very rapidly beginning at 700°C and at atmospheric pressure is capable of dissolving 1.95 atoms of H per atom of Zr. Thorium starts to absorb H_2 at 400°C; the maximum H_2 concentration corresponds to a hydride composition of $ThH_{3.24}$.

PROPERTIES:

Gray powder of somewhat lighter color and lower density than the parent metal powder. In contrast to the Ti and Zr hydrides, Th hydrides of high hydrogen content are labile and ignite spontaneously in air.

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Titanium (II) Chloride, Bromide and Iodide

$TiCl_2$, $TiBr_2$, TiI_2

Ia.

$$\underset{189.7}{TiCl_4} + \underset{47.9}{Ti} = \underset{237.6}{2\,TiCl_2}$$

A weighed quantity (2–3 g.) of $TiCl_4$ is placed with the appropriate precautions in a thick-wall quartz tube, and the stoichiometric quantity of Ti filings is added. The tube is cooled in a Dry Ice–alcohol bath, thoroughly evacuated by means of an oil pump, and melt-sealed in such a way that its total length is 12–15 cm. It is then placed in a very slightly inclined position in a tubular electric furnace so that the Ti metal is located at the higher end and the chloride at the lower. The Ti is in the hottest part of the oven (at 800–900°C), while the section containing the $TiCl_4$ is in a cooler zone (at about 200°C). An explosion shield is recommended. If one uses a mixture such as Ti + 2 $TiCl_3$ the procedure is less dangerous but more involved.

A mixture of black and purple substances ($TiCl_2$ and $TiCl_3$) is observed after 24 hours. As soon as all unreacted $TiCl_4$ disappears, the reactor tube is pushed deeper into the furnace, which results in a gradual disappearance of the reddish component. To achieve complete homogeneity, the mixture is heated for an

additional 4–5 days at 600–700°C. The product is black and may be dislodged from the wall by gentle tapping (the reaction with the quartz wall proceeds to only a very slight extent). The quartz tube is sawed open; the black powder is dropped into a transfer apparatus (Fig. 54, p. 75) and reheated in vacuum for 15–30 minutes at 200°C to remove the moisture absorbed during the transfer. The product is then ready for further processing.

Ib. To prepare larger quantities of $TiCl_2$ by the same method, it is advisable to use a vertical reactor tube, in which the molten dichloride is formed on passage of $TiCl_4$ vapor over titanium filings heated to a high temperature. A layer of Ti filings about 30 cm. high is placed on a perforated carbon plate in a fused quartz tube 110 cm. long and 4.5 cm. wide. Just underneath the carbon plate there is a graphite crucible supported by a piston-like arrangement; this crucible collects the droplets of the product. The entire arrangement is placed in a tubular furnace; the temperature at the metal level is 1050°C, while that at the level of the collecting crucible is 900°C. After thorough flushing with Ar, gaseous $TiCl_4$ is introduced from above in a slow stream of Ar. At the end of the reaction the graphite crucible is removed from the furnace in an atmosphere of a protective gas, and the solid block of $TiCl_2$ is removed by gentle tapping.

$TiBr_2$, TiI_2

These compounds are synthesized in a similar manner, except that the halogens, rather than the tetrahalides, are used as starting materials.

Ti	+	Br_2	=	$TiBr_2$;	Ti + I_2	=	TiI_2
47.9		159.8		207.7	47.9	253.8	301.7

After weighing and before addition of the Ti filings, the Br_2 must be cooled to −78°C, since liquid Br_2 and Ti react with ignition even at room temperature. This phenomenon also occurs in the sealed tube as soon as the Br_2 starts to melt. The tubes, however, are capable of withstanding the pressure. With I_2, on the other hand, the conversion to tetraiodide starts only after slight heating. In both cases, further treatment is similar to that of the chloride. The quartz tube wall is attacked even less by the bromide than with the chloride, while the iodide does not react with quartz at all.

II.

$2TiCl_3$	=	$TiCl_2$	+	$TiCl_4$
308.5		118.8		189.7

A high vacuum is created in a quartz tube, one end of which is filled with $TiCl_3$ and heated to 475°C, while the other is maintained

at −78 °C. The $TiCl_4$ formed via the disproportionation condenses at the cold end. Complete decomposition of 1 g. of $TiCl_3$ requires about 12 hours. When the reaction is over, the tube end containing the $TiCl_4$ is sealed off from the remainder. Since the decomposition reaction $2\,TiCl_3 \rightarrow TiCl_4 + Ti$ sets in below 475 °C, pure $TiCl_2$ cannot be obtained by this method; the product always contains 2–3% of free titanium.

On the other hand, this method may be very successfully used for the preparation of $TiBr_2$. At temperatures slightly above 400 °C, half a gram of $TiBr_3$ will decompose completely in 18 hours according to the equation $2\,TiBr_3 = TiBr_2 + TiBr_4$. However, the disproportionation $2\,TiBr_2 \rightarrow TiBr_4 + Ti$ sets in above 500 °C, so again free titanium may be present in the product.

III. Very pure and finely divided $TiCl_3$ may be obtained by reduction of $TiCl_4$ with H_2 in an electrical discharge produced without electrodes.

PROPERTIES:

$TiCl_3$: Black crystals; ignites in moist air; soluble in H_2O, evolving H_2 (the same properties apply to $TiBr_3$ and TiI_3). d ($TiCl_3$) 3.13, ($TiBr_3$) 4.31, (TiI_3) 4.99.

REFERENCES:

DropBooks

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II. R. C. Young and W. C. Schumb. J. Amer. Chem. Soc. 52, 4233 (1930); W. C. Schumb and R. F. Sundström. J. Amer. Chem. 55, 596 (1933); see also W. Klemm. Angew. Chem. 69, 683 (1957).

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Titanium (III) Chloride, Bromide and Iodide

$TiCl_3$, $TiCl_3 \cdot 6\,H_2O$; $TiBr_3$, $TiBr_3 \cdot 6\,H_2O$; TiI_3

$TiCl_3$

I.

$$2\,TiCl_4 + H_2 = 2\,TiCl_3 + 2\,HCl$$
$$379.4 \quad 2.0 \quad 308.5 \quad 72.9$$

a) The procedure developed by Schumb et al. was modified by Klemm and Krose as follows.

The apparatus is shown in Fig. 292. Parts *a*, *c*, and *d* are made of fused quartz, while the container *f* is Pyrex. Before the start of the reaction the entire system is thoroughly dried with a stream of H_2. About 25 g. of $TiCl_4$ is then added through *b*, the furnace is rapidly heated to 800°C, and the cooling water for the finger *d* is turned on (Schumb et al. use a system made of high-melting glass and heat to 650°C only). The $TiCl_4$ in *a* is heated almost to the boiling point while a stream of H_2 is passed through the flask; the product is free of $TiCl_3$ only if an excess of $TiCl_4$ is present in the reaction chamber. The unreacted $TiCl_4$ is collected in container *f*, which is cooled with Dry Ice. After all the $TiCl_4$ has been distilled out of flask *a*, the current to the furnace is shut off; it should cool rapidly, since the insulation consists only of a thin asbestos layer. When the temperature drops to 120°C, the water flow to the cold finger is stopped, the finger is dried with an air stream, and the furnace is kept at 120°C for several hours in order to free the product deposited on the tip of the finger of $TiCl_4$. The $TiCl_4$ left in the remaining section of the apparatus is distilled off by fanning with a flame. The system is then allowed to cool in a stream of H_2, followed by a fast stream of CO_2. The container *f* is then disconnected at *e* and replaced with a transfer device (Fig. 54, p. 75); the cork stopper carrying the cold finger is pulled out from the reactor to a distance sufficient for insertion of a scraper; the $TiCl_3$ is scraped off the finger and dropped by tapping into the transfer container. The yield of the pure product is 2-3 g.

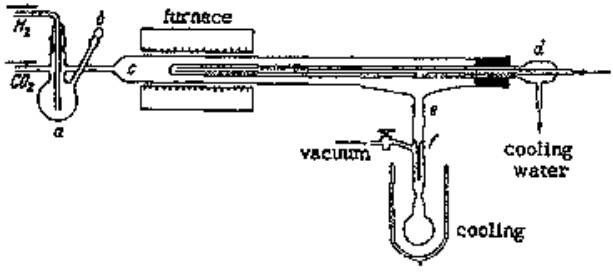

Fig. 292. Preparation of tianium (III) chloride according to Klemm and Krose. *a*) flask, *b*) charging adapter for $TiCl_4$, *c*) reaction tube, *d*) cold finger, *f*) container

b) Larger quantities (150-200 g.) of less pure product (98%) can be prepared in one day in the apparatus of Fig. 293 via reduction of $TiCl_4$ with H_2 on the surface of a glowing tungsten wire.

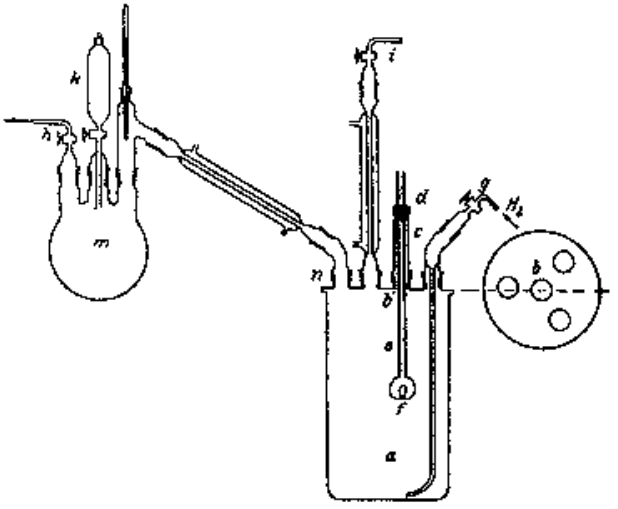

Fig. 293. Preparation of titanium (III) chloride according to Sherfey. *a*) Pyrex reactor; *e*) tungsten rods, about 6 mm. in diameter; *f*) tungsten wire coil; *m*) flask for distillation of $TiCl_4$.

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The four-liter Pyrex reaction vessel *a* is provided with a flat-ground lid with four openings, one in the middle and the other three arranged symmetrically around it. The central 34/45 ground joint *b* carries a tubular adapter *c* closed off with a two-hole rubber stopper *d* through which two tungsten rods *e* (6 mm. in diameter) are inserted. The rods are interconnected by a tungsten wire, the thickness and length of which are determined by the available power supply. Thus, heating a wire 1 mm. in diameter and 30 cm. long to the required temperature of 1000–1100°C requires a current of 36 amp. and 8.6 v. Thinner wires should not be used, if at all possible, since they may burn out during the run; longer wires increase the process rate.

The apparatus is thoroughly flushed with pure, dry H_2, which is introduced at *g* and which leaves at *h*. When all the moisture has been removed, stopcock *h* is closed and *i* is opened, without interrupting the stream of H_2. Then $TiCl_4$ (one liter = 1700 g) is introduced from dropping funnel *k* into distilling flask *m* and, except for a small residue, redistilled into the reaction vessel *a*. The distillation apparatus is then removed and the opening at *n* is rapidly closed off.

Only the lower third of reaction vessel *a* is heated with a heating mantle. The boiling $TiCl_4$ then condenses on the lid and the

side walls—cooled with a fan if necessary—and, while flowing down, washes off the nascent $TiCl_3$. If the $TiCl_4$ boils too violently, the solid $TiCl_3$ particles may come in contact with the hydrogen stream, be entrained by it and plug the reflux condenser (the condenser serves only as a safety vent).

When the boiling of the $TiCl_4$ (in the fast hydrogen stream) has reached a steady state, the tungsten wire is heated to red heat. The reduction starts immediately and is accompanied by the appearance of violet vapors of $TiCl_3$, which condense on the walls and are largely flushed down to the bottom of the $TiCl_4$-containing flask. Since there is a possibility that air may enter the system whenever there is a sudden cooling and resultant temporary vacuum, the H_2 flow rate must be carefully maintained (the air is undesirable since it may oxidize the glowing wire to the point of burnout and may also cause hydrolysis). When the $TiCl_4$ ceases to flow unhindered along the walls of the vessel, the reaction is stopped by turning off the current to the glow wire, and the flask is allowed to cool in a stream of H_2. The $TiCl_4$ may be distilled directly from the reaction beaker by replacing the lid used in the reaction with a one-hole cover. However, it is simpler to transfer the reaction mixture to a side-neck distilling flask and heat to 150°C on an oil bath. The last traces of adsorbed $TiCl_4$ are removed by heating in vacuum to 200°C; other volatile contaminants are removed at the same time. About 150 g. of $TiCl_3$, corresponding to a yield of 10% (or 90% based on the amount of $TiCl_4$ actually consumed in the reaction), is obtained. Because it contains a small quantity of $TiCl_2$, the product has a reducing value of 101.5%. It usually ignites even in moist air, and even more rapidly when it is still warm; transfer must therefore be carried out carefully, in an inert atmosphere.

The difficulties involved in welding on the tungsten coil may be circumvented by means of the following arrangement. Two copper tubes (diameter 6 mm., length about 30 cm.) are electrically insulated from each other and cemented in the adapter *c*; just above *c* they are provided with side fittings for connection to cooling water. The cement may be an epoxy resin such as Araldite 121 R with hardener 951.* The upper ends of the copper tubes, which serve as bus bars, are interconnected by means of a short piece of rubber tubing; the lower ends are closed off. A strip of molybdenum sheet (0.2 mm. thick, 6 cm. long) is soldered on at the lower end of each of the two copper tubes to support the tungsten wire. A firm electrical contact between the wire (which is wound into five or six coils) and the molybdenum strips is

*Both manufactured by the Ciba Co; see also p. 32.

achieved by threading the wire ends through a series of small holes in the strips, followed by bending the ends over and crimping to the strips.

II. $$3\,TiCl_4 + Ti = 4\,TiCl_3$$
$$^1/_{10}: \quad 56.9 \quad 4.8 \quad 61.7$$

If pure Ti metal is available, the $TiCl_3$ may be prepared in a thick-wall pressure tube made of fused quartz or Vycor in accordance with the above equation. The procedure is essentially the same as that described for the preparation of $TiCl_2$. A large amount of $TiCl_2$ forms initially; this stage may be recognized by the black color and moist appearance of the product, due to unreacted $TiCl_4$. After the initial reaction the reactor tube is gradually (over several hours) pushed completely into the furnace, which is maintained at 600°C. Should a temperature gradient exist in the system, the $TiCl_3$ will sublime, in the form of violet, leaflike crystals, into the center of the pressure tube. The tip of the tube is then broken off under a blanket of protective gas; the other end, which may contain some residual unreacted Ti, is also broken off, and the $TiCl_3$ is dropped into a transfer device (cf. Part I, p. 75), in which it is heated for an additional few minutes in vacuum to 100–150°C by fanning the vessel with a flame; the small amount of $TiCl_4$ which evolves shows that the reaction did not go to completion. The reactor walls are attacked only at the spot where the Ti metal was placed, and then only very slightly.

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III. $$3\,TiCl_4 + Sb = 3\,TiCl_3 + SbCl_3$$
$$^1/_{10}: \quad 56.9 \quad 12.2 \quad 48.3 \quad 22.8$$

The reduction of $TiCl_4$ to $TiCl_3$ with Sb does not require a complicated apparatus and may be carried out as follows:

A solution of $SbCl_3$ (d 1.265) is reduced with Zn dust. The resultant Sb is washed several times with 0.1N HCl until free of Zn, then treated with alcohol and ether, and finally dried in a stream of CO_2. Antimony prepared by other methods does not reduce $TiCl_4$ as efficiently.

Freshly distilled $TiCl_4$ (28 g.) is placed in a bomb tube and the Sb (6 g.) is added; the reactor tube is melt-sealed and heated for five hours at 340°C. After cooling, both tube ends are broken off and the moist mass, in a stream of CO_2, is transferred to a three-neck flask via an adapter at neck *a*. Then CCl_4 is added from a dropping funnel attached to neck *b* while the mixture is agitated with a stirrer inserted through the center neck; this dissolves out the unreacted $TiCl_4$. The mixture is allowed to

settle, an adjustable siphon tube is inserted at *a*, and the supernatant liquid is forced out by CO_2 pressure applied through *b*. The operation is repeated until the product is free of $TiCl_4$. The $SbCl_3$ formed in the reaction is removed in the same manner by exhaustive extraction with ether, the last traces of which are evaporated by heating on a water bath in a stream of CO_2. The $TiCl_3$, in the form of a violet powder, is transferred to storage under a blanket of CO_2. The yield is quantitative.

IV. *Alternate method:* Finely divided, very pure $TiCl_3$ may be prepared by reduction of $TiCl_4$ with H_2 in an electric arc.

$TiBr_3$

I. The preparation of $TiBr_3$ by method I*a* is similar in its essentials to that used for $TiCl_3$, except that the removal of $TiBr_4$ after completion of the reaction must be carried out at a higher temperature (250°C).

The preparation by method I*b* uses the same apparatus as that for $TiCl_3$. Since $TiBr_4$ is a solid at room temperature, the reflux condenser must be cooled with hot water or steam. The $TiBr_4$ is poured hot into the distillation flask and allowed to solidify before the apparatus is flushed with H_2.

II. Sublimed $TiBr_3$ crystals are synthesized from the elements under the same conditions as those given for $TiCl_3$.

TiI_3

II. Direct synthesis from stoichiometric quantities of the elements by heating in a sealed tube is similar to the preparation of $TiCl_3$ or $TiCl_2$ from Ti + $TiCl_4$. As long as the tetraiodide still accompanies the diiodide and the triiodide, the product is a solid cake which is difficult to break up by tapping. Toward the end of the reaction, after heating for several hours at 700°C, the product can be pulverized by vigorous shaking. The reaction may be completed at 180°C (reduce the temperature over a period of several days). The reaction is tested for completion by pulling out the tip of the tube from the furnace (maintained at this temperature) and cooling it with a piece of moist filter paper. The reaction is complete if after several hours only a very slight film of TiI_4 is observed (the film quantity is negligible compared to the total material in the reactor).

PROPERTIES:

$TiCl_3$: Formula weight 154.27. Violet-red to black crystals; sublimes in vacuum at 425–440°C; decomposes to $TiCl_2$ + $TiCl_4$

above 450°C. Readily soluble in H_2O. d 2.66. Crystal structure: type D 0_5.

$TiBr_3$: Formula weight 287.65. Bluish-black crystals; decomposes to $TiBr_2 + TiBr_4$ at 400°C. Less soluble in H_2O than $TiCl_3$.

TiI_3: Formula weight 428.66. Violet-black needle-shaped crystals; stable up to 300°C on heating in high vacuum; decomposes to $TiI_2 + TiI_4$ above 350°C. Dissolves slowly in H_2O without evolving H_2.

REFERENCES:

Ia. C. Young and W. C. Schumb. J. Amer. Chem. Soc. 52, 4233 (1930); W. C. Schumb and R. F. Sundström. J. Amer. Chem. Soc. 55, 596 (1933); W. Klemm and E. Krose. Z. anorg. Chem. 253, 209 (1947); H. Hartmann, H. L. Schläfer and K. H. Hansen. Z. anorg. allg. Chem. 284, 153 (1956); for $TiBr_3$ see also: R. C. Young and W. M. Leaders in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 116.

Ib. J. M. Sherfey. J. Research Nat. Bur. Standards 46, 299 (1951); Inorg. Syntheses, Vol. VI, New York-London, 1960, p. 57; P. Ehrlich, G. Kaupa and K. Blankenstein. Z. anorg. allg. Chem. 299, 213 (1959).

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III. M. Billy and P. Brasseur. Comptes Rendus Hebd. Séances Acad. Sci. 200, 1765 (1935).

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IronPlatBooks

$TiCl_3 \cdot 6\,H_2O$

$$\underset{189.7}{TiCl_4} \rightarrow \underset{154.3}{TiCl_3} \rightarrow \underset{262.4}{TiCl_3 \cdot 6\,H_2O}$$

Titanium (III) chloride may be prepared by cathodic reduction of $TiCl_4$ in a hydrochloric acid solution; if the concentration of $TiCl_3$ in the solution is sufficiently high, the hexahydrate precipitates on saturation with HCl. The crystallization is apparently inhibited by the presence of tetravalent titanium, and total reduction of the solution is therefore necessary.

The procedure, according to W. Fischer, is as follows.

A thick-wall cylindrical battery jar (diameter 7 cm., height 9 cm.) serves as the electrolytic cell. The center of the cell is occupied by a clay cylinder (diameter 4.5 cm., height 12 cm.). The cylinder is held in place by a cork ring with three additional holes, two for carbon anodes (placed opposite each other on the diameter) and the third for an outlet tube for the Cl_2 evolved during the electrolysis. The clay cylinder is closed with a three-hole rubber stopper, which contains an inlet tube reaching almost to the bottom of the cylinder, a short outlet tube, and a lead wire to the Pt cathode. Also recommended is the insertion of an additional glass tube, used for occasional sampling of the solution as a check on the degree of reduction.

To start with, $TiCl_4$ (19 g.) is added in drops with efficient cooling and vigorous stirring to 27 ml. of 25% HCl solution. The insoluble hydrolysis products which may be formed are filtered off through fritted glass. The clear solution is placed in the clay cylinder, and the anode chamber is filled to the same level with 25% hydrochloric acid. At 12 v. and a current density of 2.5 amp./10 $cm.^2$ of the Pt cathode, the electrolysis should require about four hours. The jar is meanwhile cooled with ice (or, if necessary, with ice-salt). Toward the end of the run, HCl is added to the solution until saturation. The hexahydrate $TiCl_3 \cdot 6H_2O$ crystallizes best when the solution is not agitated; therefore, the introduction of HCl should be interrupted for 10 minutes every half hour. If the reduction is complete, the product crystallizes within one hour, forming a solid crystalline mass. It is placed on a coarse fritted-glass filter under CO_2 and the mother liquor is removed by suction. The precipitate is washed with some saturated HCl solution, followed by ether, and the crystals are dried in a vacuum desiccator over soda lime. The $TiCl_3 \cdot 6H_2O$ then consists of small crystals.

PROPERTIES:

Pale-violet, hygroscopic crystals, readily soluble in water. Decolorizes slowly by oxidation in dry air, rapidly in moist air, with formation of white TiO_2 hydrate.

If a saturated solution of $TiCl_3$ is covered with ether and saturated with HCl, a green, very unstable isomeric hexahydrate is formed [A. Stähler and H. Wirthwein, Ber. dtsch. chem. Ges. 38, 2619 (1905)].

REFERENCE:

Private communication from W. Fischer, Hannover.

$TiBr_3 \cdot 6H_2O$

$$\underset{367.6}{TiBr_4} \rightarrow \underset{287.6}{TiBr_3} \rightarrow \underset{395.7}{TiBr_3 \cdot 6H_2O}$$

Titanium (III) bromide $TiBr_3 \cdot 6H_2O$ is prepared in exactly the same way as $TiCl_3 \cdot 6H_2O$. A solution of 37 g. of $TiBr_4$ in 25 ml of 34% hydrobromic acid is poured into the clay cylinder and reduced for three hours at a current intensity of 2.5 amp.

PROPERTIES:

Reddish-violet crystals. M.p. 115°C. Soluble in H_2O, methanol, absolute alcohol and acetone; insoluble in CCl_4 and benzene. Decomposes in absolute ether.

REFERENCES:

The same as for $TiCl_3 \cdot 6H_2O$; see also J. C. Olsen and E. P. Ryan, J. Amer. Chem. Soc. 54, 2215 (1932).

Titanium (IV) Chloride

$TiCl_4$

$$\underset{79.9}{TiO_2} + \underset{24.0}{2C} + \underset{141.8}{2Cl_2} = \underset{189.7}{TiCl_4} + \underset{56.0}{2CO}$$

PREPARATION

a) An intimate mixture of 30 g. of commercial TiO_2 (sold under the trade name "synthetic rutile"; if natural rutile is used, it must be preground for 24 hours in a ball mill until a very fine powder is obtained), 15 g. of charcoal or carbon black, and 0.05 g. of manganese dioxide catalyst is stirred to a paste with water and 0.3 g. of soluble starch. The mixture is heated in a drying chamber with occasional stirring until a material consisting of agglomerated particles is produced; this is placed in a clay crucible, covered with a layer of carbon black, and thoroughly calcined by means of a blast burner.

The chlorination is carried out in a quartz tube (20 mm. I.D.) to which an 8-mm. quartz tube is sealed at a 45° angle. The narrower tube is inserted into a 150-ml. distilling flask, which serves as the receiver.

The larger tube is charged with the $TiO_2 + C$ mixture and the entire apparatus is dried by fanning with a flame, while a stream

of CO_2 is flowing through. The receiver is immersed in an ice-salt mixture, and the reactants are slowly heated to 450°C in a stream of Cl_2. In the absence of a catalyst, or if the TiO_2 is insufficiently ground, heating to 1000°C is necessary. From time to time, particularly toward the end of the run, the tube section between the furnace and the receiver is fanned with a flame to distill off any condensed $TiCl_4$ and to prevent plugging with $FeCl_3$. At a flow rate of three liters of Cl_2 per hour, the reaction requires 4-5 hours for completion. The receiver is removed and the product $TiCl_4$ is freed of dissolved Cl_2 (and $COCl_2$, if present) by drawing a stream of dry air through the tube. The yield is about 40 g.

b) A simple laboratory apparatus, which can be used for the preparation of most anhydrous chlorides (solid, liquid and gaseous), has been described by Kroll (see Fig. 294). It is made of fused quartz, which is better than porcelain since it is attacked at much higher temperature and even then produces only a single contaminant ($SiCl_4$). The apparatus consists of a single tube in two sections, one wide and one narrow, and containing a cold finger in the large-diameter section; the latter section serves as a condensing chamber for the distillate or sublimate. The heating arrangement is divided into two parts. The heating section for the narrower tube reaches well into the wide-tube section, to prevent the chlorides from condensing in the transition section. The large-diameter section may be heated slightly if the need arises; it is only partially covered by the heating element and its exposed part may be cooled by placing it in a wooden box filled with Dry Ice; this may be necessary in the preparation of chlorides which are difficult to condense (e.g., BCl_3). Chlorides which are liquid at room temperature (e.g., $TiCl_4$) condense on the cold finger and flow into the receiver, the reactor in this case being slightly inclined. Nonvolatile chlorides deposite as solids on the finger.

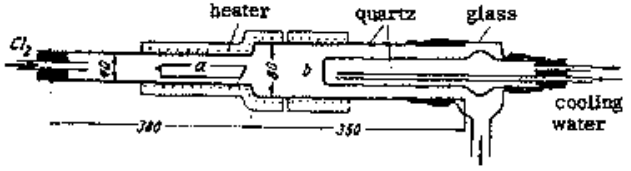

Fig. 294. Preparation of anhydrous chlorides according to Kroll. The main tube and the cold finger are made of fused quartz. *a*) reaction chamber; *b*) condensing chamber. Dimensions in mm.

If the raw materials for $TiCl_4$ are very pure TiO_2 and sugar charcoal calcined in a stream of Cl_2, then the prepurification

described below becomes unnecessary. The solid charcoal may be dispensed with if the chlorine stream also contains CCl_4 or S_2Cl_2.

See also the preparation of $ZrCl_4$.

PREPURIFICATION

The crude product is decolorized and contaminants such as $FeCl_3$, $VOCl_3$, etc., are removed by adding 1 g. of Cu *powder* (Na amalgam or Hg may also be used) and heating the liquid to 90–100°C for 15 minutes with occasional shaking.

[If Cu *turnings* are used, the amount specified above must be increased tenfold. Oleic acid and its salts and other organic compounds, in quantities of less than 1%, are also efficient decolorizing agents [C. K. Stoddard and E. Pietz, U. S. Bur. Mines Rep. Invest. 4153, 40 (1947)].

According to British Patent 588,657 the following purification procedure is particularly well suited for the removal of traces of vanadium. The product containing 0.072% V is mixed with 0.1% of Fe stearate and treated with H_2S, causing precipitation of a black-brown sulfide; the latter is filtered off. The $TiCl_4$ then contains only 0.002% V.]

After heating with copper, the $TiCl_4$ is cooled and suction-filtered through a very dry filter funnel, and the filtrate is transferred for further purification (removal of $SiCl_4$ and dissolved nonvolatile hydrates) to the distillation apparatus described below (Fig. 295).

A) ATMOSPHERIC PRESSURE DISTILLATION

The neck of distilling flask *a* is closed off with a ground stopper provided with a small hook, from which a thermometer is suspended on a Pt wire. The side arm passes through a condenser jacket; a small bulb *b* (the receiver for the forerun) and an outlet tube *c* filled with P_2O_5 are sealed on as shown. In the initial stage of the run, the system ends in a second distilling flask *e* equipped with a break-seal valve *f* (see Part I, p. 63), via which the flask is later connected to additional pieces of glassware. The apparatus is set up to point *i* and flasks *a* and *e* are dried by fanning with a flame while a stream of air is passed through. Then $TiCl_4$ is placed in flask *a* and the latter is heated on an oil bath. The forerun is collected in *b*, which is then sealed off, while the main fraction of the material is distilled into *e*, which is then sealed off at *d*. This operation is followed by an additional distillation at atmospheric pressure: flask *e* is melt-sealed at *i* to the system shown on the right side of Fig. 295A; this part of the apparatus is very thoroughly dried by alternately evacuating the apparatus and allowing dry air to enter. The thin-wall break-seal

valve is then shattered at the prescratched point g by moving the hammer h by means of a magnet. The forerun from this distillation is collected in k and the main fraction of the distillate in receiver m, which is then melt-sealed at point l.

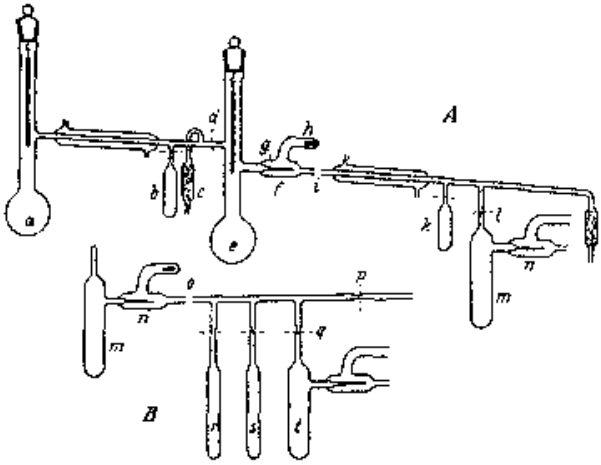

Fig. 295. Purification of titanium (IV) chloride by distillation: *A*) at atmospheric pressure; *B*) in vacuum.

B) VACUUM DISTILLATION

Vessel m is melt-sealed at o to the rest of the apparatus shown in Fig. 295B, and the entire system is dried by fanning with a flame while a high vacuum is maintained. The $TiCl_4$ is then introduced into m and frozen with liquid nitrogen, the break-seal valve n is broken by the method described above, the system is evacuated to 10^{-4} mm. and sealed at p. A forerun is collected in r by cooling this trap and gradually heating flask m; the connection to r is then sealed off. The main fraction of the product may now be distilled in one batch, that is, by collecting in cooled receiver t, sealing off at q, and repeating the vacuum distillation; or the $TiCl_4$ may be distributed into several batches and collected in traps s_1, s_2, s_3, etc.

PROPERTIES:

Colorless, acrid liquid; fumes strongly in moist air. M.p. −24.8°C, b.p. 136°C; d 1.73.

Hydrolyzes almost completely on solution in water; if the **hydrolysis** is depressed by addition of acid or if only small

quantities of water are used, oxychlorides may form as intermediates. Readily forms adducts with ammonia, pyridine, nonmetal chlorides, etc.

REFERENCES:

Preparation: a) Private communication from W. Fischer, Hannover. b) W. Kroll, Metall u. Erz 36, 101, 125 (1939); see also A. Köster, Angew. Chem. 69, 563 (1957).
Prepurification: A. V. Pamfilov, A. S. Chudyakov and E. G. Standel, Zh. Prikl. Khimii 142, 232 (1935), and other papers of A. V. Pamfilov published in that period.
Distillation: K. Arii, Sci. Rep. Tohoku Imp. Univ. 22, 959 (1933); the apparatus described may be used for the distillation of other highly corrosive liquids, such as $POCl_3$, $SOCl_2$, etc.
Purification of $TiCl_4$ for atomic weight determinations is described by G. P. Baxter, J. Amer. Chem. Soc. 45, 1228 (1923); 48, 3117 (1926); E. H. Archibald, The Preparation of Pure Inorganic Substances, New York, 1932, p. 184.

Ammonium Hexachlorotitanate

$(NH_4)_2[TiCl_6]$

This is a good, easily measured starting material for preparing hydrochloric acid solutions of titanium, since it forms concentrated, stable solutions in water or dilute hydrochloric acid.

$$\underset{189.7}{TiCl_4} + 2\,\underset{107.0}{NH_4Cl} = \underset{290.7}{(NH_4)_2[TiCl_6]}$$

The preparation comprises precipitation of $(NH_4)_2[TiCl_6]$ from an HCl-saturated solution, using a special apparatus which may also be employed in many other syntheses.

A 200-ml. wide-neck Erlenmeyer flask is used to hold 100 ml. of solution. The flask is closed off with a closely fitting three-hole rubber cap ("fermentation cap"). A glass stirrer, preferably of the twist drill type, is inserted in the center hole; a drop of glycerol is used for lubrication and gas seal. The use of a ground joint sealed to a mercury-seal agitator is also recommended. Laborious centering of the stirrer is avoided and easy assembly and dismantling of the apparatus promoted by coupling the stirrer to the motor shaft (or the speed reducer shaft) by means of a piece of strong, rigid rubber vacuum hose. The direction of rotation of the stirrer is such that the center of

the liquid is pushed down; higher agitation rates can be reached with this arrangement without danger of splashing, and the stirring is also more efficient.

The flask is supported at the neck by a clamp which holds it in a cooling bath at a depth so that it is covered with coolant to just below the clamp level while still leaving enough coolant underneath the flask to provide cooling of the bottom.

The gas inlet tube need not dip into the solution, since the rate of absorption of HCl in the vigorously stirred liquid is so rapid that it is almost controlled by the input rate alone; possible plugging of the inlet tube is also avoided by not letting the tube dip into solution. The HCl addition rate is controlled to avoid the formation of a mist above the stirred mixture, a point at which evaporation losses just begin. The greater the stirring rate, the higher the rate at which the HCl may be introduced, and the sooner the end of the run. Complete saturation of 100 ml. of precipitation solution requires less than one hour.

The HCl flow rate is sharply reduced toward the end of the run. The progress and termination of the HCl absorption can be followed by means of bubble counters inserted ahead of and behind the precipitation flask.

The HCl generator must be capable of yielding a continuous stream of gas and must also allow a wide range of adjustment in the flow rate; in addition, it should be easy to start, give an air-free gas stream as soon as possible after the start, and stop generating gas shortly after being turned turned off. The generator described on p. 280 fulfills these conditions less well than the apparatus developed by W. Seidel [Chem. Fabrik 11, 408 (1938)], in which conc. hydrochloric and conc. sulfuric acids react to give a good yield of HCl; this is accomplished by dropping the acids separately onto a packing of glass beads.

If only small quantities of HCl are required, the most convenient generator is still the Kipp, which utilizes the reaction of conc. sulfuric acid with lumps of NH_4Cl, particularly since the gas does not have to be dried. However, foaming is quite pronounced at larger HCl flows.

Returning now to the precipitation of $(NH_4)_2[TiCl]_6$, gaseous HCl is introduced at 0°C into a solution of 6 g. of $TiCl_4$ in 100 ml. of aqueous (7:1) hydrochloric acid containing about 4 g. of NH_4Cl. The HCl gas is added until saturation. Then the HCl flow is stopped, but stirring is continued until complete precipitation. If the precipitation rate is low, the yellow $(NH_4)_2[TiCl_6]$ is obtained in the form of coarse crystals averaging 0.1 mm.

The precipitate is separated from most of the mother liquor by a short suction filtration through coarse fritted glass (without allowing air to be drawn through the compound), and the crystals are then pressed between two pieces of filter paper. If an asbestos

filter is used, the compound must be repeatedly boiled with conc. hydrochloric acid and then very thoroughly washed.

PROPERTIES:

Yellow octahedra, probably of the $K_2[PtCl_6]$ structure. May be stored for an indefinite period if moistened with hydrochloric acid and kept in a closed container; on washing with anhydrous ether and drying over conc. H_2SO_4 in a vacuum desiccator, decomposes with pronounced evolution of HCl. In moist air, forms a white hydrolysis product, which is unusual in still being soluble in water.

REFERENCES:

A. Rosenheim and O. Schütte, Z. anorg. Chem. 26, 239 (1901); W. Fischer and W. Seidel, Z. anorg. allg. Chem. 247, 333 (1941); W. Seidel and W. Fischer, Z. anorg. allg. Chem. 247, 367 (1941).

Titanium (IV) Bromide

$TiBr_4$

DropBooks

I.

$$TiCl_4 + 4\,HBr = TiBr_4 + 4\,HCl$$

189.7 323.7 367.8 145.8

Due to the long time required (30 hours), the original method described by Thorpe in 1856 (bubbling of HBr through warm $TiCl_4$ until the boiling point of the solution equals that of $TiBr_4$) has been modified as follows.

Receiver *b* of the apparatus shown in Fig. 296 is cooled with liquid nitrogen or Dry Ice, and pure, dried HBr is condensed in until enough liquid is present. The section above *d* is then broken off, $TiCl_4$ is added to *a*, and the apparatus is resealed at *e*. Stopcock *f* is closed, *i* is opened, and $TiCl_4$ is slowly distilled into container *b*, which is cooled with Dry Ice; the initial reaction is quite violent. By periodically removing the coolant, it is possible to bring the reaction to completion. The gas mixture evolved (essentially HCl) is vented through stopcock *i*, while the HBr is condensed in *c* by proper cooling. The mixture is allowed to warm up to room temperature in order to accelerate the reaction, and the condensation of fresh HBr into the flask is repeated several times. Finally, vessel *b*, which contains an already very pure crude product, is sealed off at *g*; if desired, flask *c* may be sealed at point *h* to a distillation apparatus (such as the one described

in the preparation of TiI_4) and the $TiBr_4$ further purified by vacuum distillation.

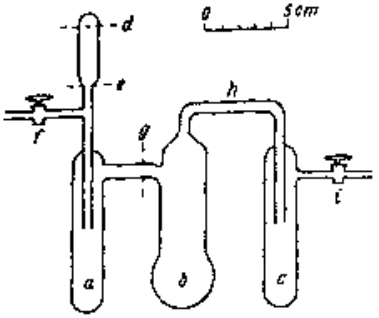

Fig. 296. Preparation of titanium (IV) bromide.

II. $$TiO_2 + 2C + 2Br_2 = TiBr_4 + 2CO$$
$$79.9 \quad 24.0 \quad 319.7 \quad 367.6 \quad 56.0$$

The already-described method of preparation of $TiCl_4$ is modified only to the extent that the stream of Cl_2 is replaced by dry CO_2 which passes through a 60°C wash bottle containing 135 g. of Br_2; the bromine-saturated CO_2 then passes over the reaction mixture (30 g. of TiO_2 + 15 g. of wood charcoal), which is heated to about 600°C. A mixture of $TiBr_4$, CBr_4 and free Br_2 collects in the receiver. The last two products are distilled off in a stream of pure CO_2 bubbled through the melt, leaving the $TiBr_4$ as the residue. Cooling to room temperature produces a solid mass, which may be purified by multiple distillation. The yield is 80%.

III. $$Ti + 2Br_2 = TiBr_4$$
$$47.9 \quad 319.7 \quad 367.6$$

If metallic Ti is available, the compound may be easily synthesized from the elements (see the procedure for the preparation of titanium dihalides). A weighed amount (5–6 g.) of freshly distilled Br_2 is placed in a thick-wall quartz tube cooled with Dry Ice, crude Ti is added (somewhat more than the stoichiometric quantity), and the tube is sealed under high vacuum. The Br_2 begins to melt on removal of the coolant; the reaction starts immediately and flames appear. After completion of the reaction the tube is opened and the $TiBr_4$ is distilled off; it may be purified by multiple distillation (see TiI_4).

PROPERTIES:

Amber yellow, octahedral crystals. M.p. 40°C, b.p. 230°C; d 3.25. Extremely hygroscopic, absorbs moisture with hydrolytic decomposition. Very readily soluble in alcohol, moderately in ether; soluble in 34% hydrobromic acid and in conc. hydrochloric acid. Crystal structure: type $D1_1$.

REFERENCES:

I. W. Biltz and E. Keunecke, Z. anorg. allg. Chem. 147, 171 (1925); W. Klemm, W. Tilk and S. von Müllenheim, Z. anorg. Chem. 176, 1 (1928).
II. See also J. C. Olsen and E. P. Ryan, J. Amer. Chem. Soc. 54, 2215 (1932), as well as R. C. Young in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 114.
III. See also J. M. Blocher Jr., R. F. Rolsten and I. E. Campbell, J. Electrochem. Soc. 104, 553 (1957).

Purification of $TiBr_4$ for atomic weight determination is described by G. P. Baxter and A. Q. Butler, J. Amer. Chem. Soc. 50, 408 (1928); E. H. Archibald, The Preparation of Pure Inorganic Substances, New York, 1932, p. 185.

DropBooks

Zirconium (IV), Hafnium (IV) and Thorium (IV) Chlorides and Bromides

$ZrCl_4$, $HfCl_4$, $ThCl_4$; $ZrBr_4$, $HfBr_4$, $ThBr_4$

$ZrCl_4$

$$\underset{123.2}{ZrO_2} + \underset{24.0}{2\,C} + \underset{141.8}{2\,Cl_2} = \underset{233.0}{ZrCl_4} + \underset{56.0}{2\,CO}$$

An intimate mixture of one part of pure ZrO_2 and two parts of calcined carbon black or sugar charcoal is placed in a porcelain boat and heated at 500°C in a stream of Cl_2; or, preferably, ZrO_2 with no admixtures is chlorinated in a Cl_2-CCl_4 gas mixture produced by passing Cl_2 through a wash bottle (70°C) filled with CCl_4. The initial chlorination temperature is 350°C, but is gradually raised to 700°C.

The equipment is similar to that described on p. 889 for the preparation of $BeCl_2$, except that, when working with Cl_2-CCl_4, a trap for the unreacted CCl_4 must be inserted in line after tube A. Since $ZrCl_4$, which sublimes at 331°C, is difficult to recondense, it is advisable to use a long tube (600 mm.), preferably of Vycor. The additional resublimation at 300-350°C is carried out in a stream of H_2, a treatment which more effectively removes the oxide and $FeCl_3$ present.

Alternate method: The industrial chlorination of ZrC prepared from $ZrSiO_4$ is described by W. J. Kroll et al. [Trans. Electrochem. Soc. 89, 265 (1946); 92, 187 (1947); J. Electrochem. Soc. 94, 1 (1948)].

PROPERTIES:

White crystalline powder. Sublimation point 331°C, m.p. (under pressure) 438°C; d 2.80. Yields a mist of hydrochloric acid in moist air; violently decomposed by H_2O, forming the oxychloride. Soluble in alcohol and ether. Crystal structure: type D 1_1.

$HfCl_4$, $ThCl_4$

The same general method is used for $HfCl_4$ and $ThCl_4$; in the case of $ThCl_4$, the Cl_2-CCl_4 mixture should be replaced with Cl_2-SCl_2, since this allows reducing the temperature to 700°C instead of 900°C.

$ZrBr_4$, $HfBr_4$, $ThBr_4$

The preparation of the bromides in a Br_2-saturated nitrogen stream requires high temperatures if practical reaction rates are to be achieved. The oxide-carbon mixture must usually be heated to about 1100°C; this temperature is easily attained with a gas-air blast burner provided the quartz reactor is embedded in porous, refractory gravel ("Diatomite" gravel).

The preparation of $HfBr_4$ and the lower bromides $HfBr_3$ and $HfBr_2$ is described in W. C. Schumb and C. K. Morehouse, J. Amer. Chem. Soc. 69, 2696 (1947).

REFERENCES:

D. Lely and L. Hamburger, Z. anorg. Chem. 87, 209 (1914); A. Voigt and W. Biltz, Z. anorg. allg. Chem. 133, 277 (1924); O. Hönigschmid, E. Zintl and F. González, Z. anorg. allg. Chem. 139, 293 (1924); J. H. deBoer and J. D. Fast, Z. anorg. allg. Chem. 187, 177 (1930); W. Fischer, R. Gewehr and H. Wingchen, Z. anorg. allg. Chem. 242, 161 (1939); J. P. Coughlin and E. G. King, J. Amer. Chem. Soc. 72, 2262 (1950); for the bromides, see also R. C. Young and H. G. Fletcher in: H. S. Booth, Inorg. Syntheses, Vol. I, New York-London, 1939, pp. 49, 51.

Thorium Chloride

$ThCl_4 \cdot 8\,H_2O$

A solution of thorium hydroxide in excess hydrochloric acid is evaporated until sirupy and is then allowed to cool and crystallize.

Further purification, in particular, removal of Fe and SiO_2, is best achieved by shaking with an ether–aqueous hydrochloric acid mixture. The experimental arrangement is the same as described for the preparation of $(NH_4)_2[TiCl_6]$, p. 1199.

The crystals are dissolved in the minimum quantity of 6N HCl, filtered through asbestos, and shaken twice with ether to remove the iron. Silicic acid precipitates during the evaporation and is also filtered off. The filtrate is cooled to 0°C, and HCl gas is passed through until saturation. An equal volume of ether is added and the mixture is treated with additional HCl until homogeneous. Pure white crystals of $ThCl_4 \cdot 8\,H_2O$ crystallize; these are filtered, washed with ether, and dried.

PROPERTIES:

Formula weight 518.08. Deliquescent in moist air, readily soluble in water and alcohol. Soluble in ethylenediamine.

REFERENCES:

C. B. Kremer. J. Amer. Chem. Soc. 64, 1009 (1942); T. Muniyappan, Master's Dissertation, University of Illinois, 1955.

DropBooks

Titanium (IV), Zirconium (IV) and Thorium (IV) Iodides

TiI_4 (ZrI_4, ThI_4)

Syntheses I and II (described below) start from crude Ti (prepared from $TiCl_4$ and Na), which is allowed to react with I_2 vapor, while in method III a commercial fine Ti–Al alloy powder (Altam 70%, i.e., containing 70% Ti) is boiled in a solution of I_2 in CS_2. Upon removal of the solvent, the AlI_3 is bound in a nonvolatile complex $KAlI_4$, while the TiI_4 is distilled off. This method is recommended for larger-scale preparations.

$$\underset{47.9}{Ti} + 2\underset{507.7}{I_2} = \underset{555.6}{TiI_4}$$

I. Crude Ti (20 g.) is treated with dilute hydrofluoric acid, washed with distilled water and alcohol, and dried. It is then placed in the center bulb *e* of the apparatus shown in Fig. 297, which is sealed off at *f* as close to the bulb as possible. The apparatus is made of high-melting glass, preferably fused quartz ware if highest purity is to be obtained. Filling tube *a* is closed off with a rubber stopper; the system is evacuated and dried by fanning with a flame while vacuum is maintained. The stopper at *a*

Fig. 297. Preparation of titanium (IV) iodide according to the method of Blocher and Campbell.

is removed for a while, and doubly sublimed, carefully dried I_2 (100 g.) is added via tube *a*. The I_2 is melted and transferred as a melt into bulb *c*, which is then sealed off at *b*. Bulb *c* is cooled with Dry Ice; the system is evacuated to 10^{-3} mm. and sealed at *i*. The center bulb is heated to 525°C, and the two side bulbs are alternately heated and cooled with air, to produce a slow stream of I_2 vapor which flows back and forth over the heated metal. The reaction is complete after three passes. The conversion is quantitative, based on the metal content of the Ti. Nonmetallic impurities are left as a residue in *e*. If the compound is to be resublimed or subdivided into portions, additional bulbs are fused onto *h* as described in the preparation of $BeCl_2$ (p. 889).

II. If a particularly pure product is desired, one may proceed as follows: 2 g. of Ti powder is placed in section *a* of the Pyrex apparatus shown in Fig. 298 and heated for one hour at 500°C in high vacuum (provided by a pump attached at *o*). The material is then cooled to room temperature, and thin glass partition *d* is broken by means of a magnet and steel ball *g* (which is then removed from the system by sealing off at *h*); bulb *b*, which contains 10 g. of I_2, is thus connected to the rest of the apparatus. The latter is now sealed off at *i* and the pump is turned off. The I_2 vapor reacts immediately (sometimes slight heating is necessary) with the Ti to give a quantitative yield of TiI_4 (in the preparation of ZrI_4, it is necessary to heat the apparatus for several hours in an electric furnace at 200°C). When the reaction is complete, the apparatus is sealed off at *m*. After breaking partition *f*, the gases liberated during the reaction are removed by means of a high-vacuum pump connected at *q*. The system is resealed at *k*, the TiI_4 is sublimed from *a* into *c* by heating the former, and constriction *n* is sealed off. The pump may now be connected at *p*, *e* broken, and any gas

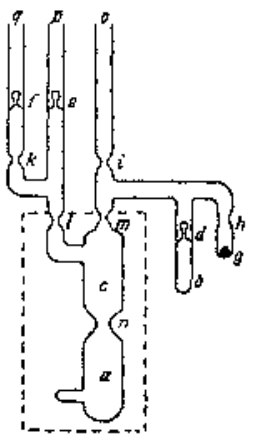

Fig. 298. Preparation of titanium (IV) iodide according to Fast: *d*, *e* and *f* are break-seal valves; *g* is a steel ball.

evolved during the sublimation removed. The compound may then be removed, as desired, through *p*. If the TiI_4 is to be stored, the system is sealed off at *l*.

The preparation of ZrI_4 or ThI_4 is similar.

III. In the method of Blumenthal and Smith, the apparatus (Fig. 299) consists of a two-liter, long-neck, round-bottom flask *a*, two smaller round-bottom flasks *b* and *c* (500 ml., 250 ml. respectively), a condenser and a receiving flask *d* (250 ml.). The multihole rubber stopper in the large flask carries the following: 1) an annular heating device consisting of a glass tube *g* which terminates at the bottom in a closed sphere; steam is introduced via a thin inner rubber tube which reaches down to the sphere; 2) a dropping funnel; 3) a reflux condenser; and 4) a glass tube with a larger-diameter filter section (the latter is in flask *a* and is filled with glass wool). All openings to the atmosphere are protected with drying tubes filled with silica gel. Before the start of the preparation, 10 g. of KI is placed in flask *b*. The apparatus is assembled and dried by fanning with a flame while a stream of air is drawn through. The rubber stopper is raised rapidly and 127 g. of I_2, dissolved in 600 ml. of CS_2, and 50 g. of finely powdered Altam 70% alloy (equivalent to 1/2 mole of free Ti, the remainder being the oxide) is added to flask *a*. The solution is brought to a boil by passing steam through the heating device. The heating is

DropBooks

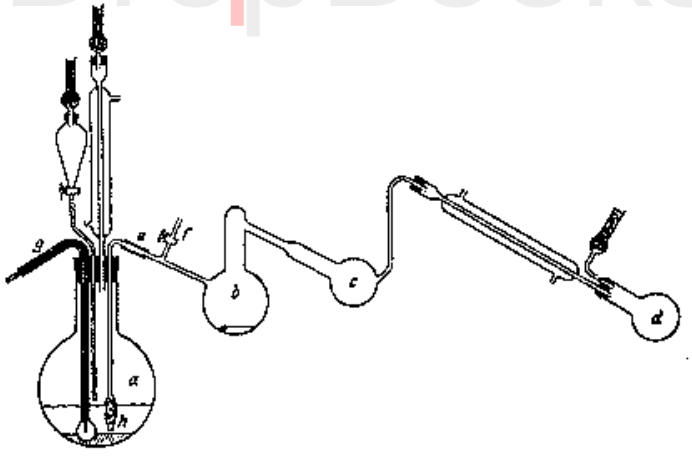

Fig. 299. Preparation of titanium (IV) iodide according to Blumenthal and Smith: *e* rubber connection with pinchcock; *g* steam heater consisting of an outer glass tube with a sphere and an inner rubber tube; *h* filter with glass wool packing.

continued for one hour with occasional shaking, resulting in quantitative formation of the iodides (TiI_4 and AlI_3). These are soluble in CS_2.

The mixture is cooled to room temperature and compressed dry air is introduced via the reflux condenser, forcing the solution through the glass wool filter and into flask *b*. This transfer is carried out in stages, since the iodide solution in flask *b* must be concentrated from time to time by distilling excess CS_2 into flask *d*. Finally, three 100-ml. portions of CS_2 are added to rinse out the last traces of product in *a*; these are also transferred to *b*.

The rubber connection *e* is closed off with a clamp and flask *a* is removed from the system. Flasks *b* and *c* are heated in a water bath to 80°C until all the CS_2 distills into *d*. A slow stream of dry N_2 is introduced through stopcock *f*, and flask *b* is strongly heated with a burner while flask *c* is cooled with cold water; this causes the AlI_3 to react quantitatively with the KI to form nonvolatile $KAlI_4$; the TiI_4 meanwhile distills into *c*. The distillation is ended when colored vapors can no longer be observed.

The crude product (90% yield) contains 95.1% TiI_4, 4.6% free I_2 and 0.3% iodides of other metals. Since 98% of the CS_2 is recycled, and since KI and I_2 may be recovered from the $KAlI_4$ melt by air oxidation:

$$4\,KAlI_4 + 3\,O_2 = 4\,KI + Al_2O_3 + 6\,I_2,$$

the process is suited for the preparation of large quantities of TiI_4.

IV. *Alternate method:* If metallic Ti is not available, TiI_4 may be prepared by the method of Hautefeuille (1867). The procedure is similar to method I for the preparation of $TiBr_4$.

The tetraiodides of Ti, Zr and Th may be produced from the oxides with the aid of AlI_3.

PROPERTIES:

Red-brown octahedra crystallizing in type D 1_1, but transformed on prolonged storage to a modification with a lower degree of symmetry. M.p. 150°C, b.p. 377°C; d 4.40. Fumes strongly in air; dissolves rapidly in water with hydrolytic decomposition.

REFERENCES:

I. J. M. Blocher and I. E. Campbell, J. Amer. Chem. Soc. 69, 2106 (1947); V. Gutmann and H. Tannenberger, Monatsh. Chem. 87, 423 (1956).
II. J. D. Fast, Z. anorg. allg. Chem. 239, 146 (1938).
III. W. B. Blumenthal and H. Smith, Ind. Eng. Chem. 42, 248 (1950).
IV. W. Biltz and E. Keunecke, Z. anorg. allg. Chem. 147, 171

(1925); W. Klemm, W. Tilk and S. von Müllenheim. Z. anorg. allg. Chem. 176, 1 (1928); M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. 242, 263 (1956); S. Ramamurthy. J. Sci. Industr. Res. 14B, No. 8, 414.

Titanium (III) Oxychloride

TiOCl

$$\underset{79.9}{TiO_2} + 2\,\underset{308.5}{TiCl_3} = 2\,\underset{198.7}{TiOCl} + \underset{189.7}{TiCl_4}$$

A quartz tube is thoroughly baked while under high vacuum. It is then charged (under a nitrogen blanket) with $TiCl_3$ (50% excess) and TiO_2. The tube is evacuated (10^{-5} mm.), sealed off and placed in a furnace with a temperature gradient so that one third of the tube, containing the TiO_2-$TiCl_3$ mixture, is at 650°C while the remainder is at 550°C. The reaction ends in about 12 hours; the excess $TiCl_3$ and a small amount of yellowish-brown crystals of TiOCl pass into the cold zone. The hot zone contains a brown, finely crystalline cake of TiOCl. If heating in the temperature gradient is continued for several days all of the TiOCl migrates to the colder zone and deposits as beautiful long crystals. The TiOCl is isolated by distilling the $TiCl_4$ into the empty half of the tube, freezing it there, and cutting the tube in two. The mixed crystals of TiOCl and $TiCl_3$ are then treated with dimethylformamide, in which $TiCl_3$ dissolves readily, forming a blue solution. The TiOCl residue is repeatedly washed with dimethylformamide, followed by alcohol and ether, and dried in vacuum.

The compound may also be prepared by a similar procedure via the reaction of $TiCl_3$ with Fe_2O_3, SiO_2, H_2O or O_2.

PROPERTIES:

Golden-yellow to red-brown crystals; decomposes slowly in air. Decomposes to TiO_2 and $TiCl_4$ on heating in an open annealing tube.

REFERENCE:

H. Schäfer, F. Wartenpfuhl and W. Weise, Z. anorg. allg. Chem. 295, 268 (1958).

Titanium (IV) Oxychloride

$TiOCl_2$

I. $$\underset{189.7}{3\,TiCl_4} + \underset{197.8}{As_2O_3} = \underset{134.8}{3\,TiOCl_2} + \underset{181.3}{2\,AsCl_3}$$

An excess of $TiCl_4$ is treated with As_2O_3, resulting in a highly exothermic reaction which goes to completion if caking of the

solid product is avoided. The yellowish substance obtained is freed of $AsCl_3$ and excess $TiCl_4$ by suction filtration in the absence of air and thorough washing with absolute pentane or CCl_4. Residual solvent is removed by vacuum distillation at room temperature. The product contains traces of arsenic.

II. $$\underset{189.7}{TiCl_4} + \underset{86.9}{Cl_2O} = \underset{134.8}{TiOCl_2} + \underset{141.8}{2\,Cl_2}$$

A stream of Cl_2O diluted with dry O_2 is introduced through a large-diameter inlet tube into a two-neck 250-ml. flask containing about 100 ml. of $TiCl_4$ (the $TiCl_4$ is distilled into the flask under conditions of complete exclusion of moisture). The gas is prepared by passing a stream of O_2-Cl_2, predried with P_2O_5, over HgO. The latter is contained in a glass tube provided with a cooling jacket and able to rotate (Liebig condenser).

Plugging of the inlet tube with solid $TiOCl_2$ is prevented by sealing a glass spatula to the bottom of the flask in such a way that it projects a few centimeters into the tube. Occasional rotation of the flask around the inlet tube then keeps the latter free.

The O_2-Cl_2O mixture is bubbled in until the formation of a crystalline paste makes this impossible. The mixture is allowed to stand overnight, whereupon any small quantity of hypochlorite still present decomposes to Cl_2 and additional $TiOCl_2$. The product is filtered in the absence of moisture and washed several times with high-purity CCl_4 which has been distilled over P_2O_5; the product is freed of the CCl_4 by evaporating the latter in a stream of a dry gas, and is then kept in vacuum for a short time.

The yield is practically quantitative, based on Cl_2O; based on $TiCl_4$ actually used, it is about 50%.

PROPERTIES:

Pale yellow, hygroscopic, crystalline powder. Sparingly soluble in CCl_4, benzene and similar solvents, moderately soluble in ethyl acetate, readily soluble in ethereal hydrochloric acid (decomposition). Hydrolyzes in moist air, giving a white color. Dissociation to $TiCl_4$ and TiO_2 begins at 180°C. d 2.45.

REFERENCES:

I. P. Ehrlich and W. Engel, Z. anorg. allg. Chem. 322, 217 (1963).
II. K. Dehnicke, Angew. Chem. 75, 417 (1963); Angew. Chem. (International Ed. in English) 2, 325 (1963).

Zirconium Oxychloride

$ZrOCl_2 \cdot 8\,H_2O$

The anhydrous compound is unknown. Of the existing hydrates, with 2, 2, 5, 6 and 8 moles of H_2O, the last is the most important,

since it crystallizes as a sparingly soluble compound from aqueous solutions containing HCl. In a solution containing about 1.2 g. of $ZrOCl_2 \cdot 8H_2O$ per 100 ml. of H_2O, the flat minimum section of the solubility curve corresponds to a concentration of 7–8 moles of HCl/liter at 0°C. The octahydrate is readily recrystallized and can therefore be prepared in very pure form.

PREPARATION

$$\underset{123.2}{ZrO_2} \rightarrow \underset{322.3}{ZrOCl_2 \cdot 8H_2O}$$

I. Since zircon $ZrSiO_4$, a mineral found in nature, is more difficult to work with, it is better to start from zirconia ZrO_2 (baddeleyite), which is calcined, finely ground (the coarser particles are screened off with silk gauze), and converted to the sulfate by evaporation or treatment for several days with an excess of warm conc. H_2SO_4. The solid residue, which consists of $Zr(SO_4)_2$ and unreacted ZrO_2, is taken up in water (the solid is added in small portions to prevent heating of the solution). The sulfate dissolves slowly, and its solution may be aided by acidifying the water with some hydrochloric acid. The resultant milky suspension, which contains solid undissolved ZrO_2 and SiO_2 (or $ZrSiO_4$), is allowed to stand for several hours and filtered.

The weakly acidic sulfuric acid solution is precipitated with ammonia and the hydroxide is filtered off. If the precipitate still exhibits a high Si content, it is dissolved in conc. hydrochloric acid and the solution is evaporated to dryness; this procedure is repeated several times. On redissolving in water, SiO_2 and some basic zirconium chloride become the insoluble residue. If no Si is evident in the hydroxide, the fresh gel is dissolved in cold hydrochloric acid and the oxychloride is allowed to crystallize by adding conc. hydrochloric acid or saturating with HCl. The crystals are filtered and washed with 8N HCl.

II. When the starting material is high in SiO_2 and, in general, if a platinum dish is available, the ZrO_2 may be evaporated with a mixture of conc. H_2SO_4 and 40% hydrofluoric acid instead of with pure H_2SO_4. The temperature required for this procedure is lower than in the preceding method. The subsequent steps are as described in method I.

III. The octahydrate $ZrOCl_2 \cdot 8H_2O$ may also be prepared as follows. A suspension of freshly precipitated zirconium hydroxide in H_2O is dissolved in cold dilute hydrochloric acid; after filtering, the $ZrOCl_2 \cdot 8H_2O$ is crystallized by evaporation (if necessary, by

adding conc. hydrochloric acid). The starting zirconium hydroxide is prepared by precipitating a solution of K_2ZrF_6 with ammonia; the precipitate, which contains a basic fluoride, must be treated for a short time with conc. H_2SO_4 (to remove the HF) and redissolved in H_2SO_4. The pure hydroxide is precipitated with ammonia.

IV. $ZrCl_4$ is dissolved in water (do not heat to dissolve—if necessary, add some hydrochloric acid); the solution is filtered and the oxychloride is precipitated by making the solution 7–8N in HCl.

The crude chlorination products of those zirconium-containing minerals that are difficult to break down must be rechlorinated with Cl_2 at 1000°C, yielding crude chlorides, which can then be purified via method IV.

PREPARATION BY RECRYSTALLIZATION OF THE OXYCHLORIDE

V. The fact that $ZrOCl_2 \cdot 8H_2O$ dissolves readily in water and is insoluble in 7–8N (25–30%) hydrochloric acid allows this compound to be used as an intermediate in the purification of Zr salts. Although complete isolation of zirconium cannot be achieved, this method eliminates not only Al, Fe, Nb, Ta, the rare earths and many other elements, but also Ti, the removal of which otherwise involves great difficulties. Thus, for example, the Al content may be reduced from 0.035% to 0.0015% by only one recrystallization; the decrease in Fe content is of the same order of magnitude. Reprecipitation of the oxychloride is thus more effective than that of the sulfate, described on p. 1232.

Since the molar solubility of $HfOCl_2 \cdot 8H_2O$ is identical to that of the Zr salt, the Hf/Zr ratio remains unchanged.

The strongly acidic HCl solution of $ZrOCl_2 \cdot 8H_2O$ is evaporated on a water bath until crystallization is incipient and is then treated with an equal volume of conc. hydrochloric acid; the mixture is heated (do not allow too much HCl to escape) and, if necessary, 25% hydrochloric acid is added to the warm mixture until solution is complete and the mixture contains, at most, 39 g. of oxychloride, i.e., 15 g. of ZrO_2 per 100 ml. The solution is mechanically stirred and its temperature is allowed to drop to a point where it still feels warm to the hand; it is then cooled with ice. After stirring for 30 minutes at 0°C, the product is filtered through a medium-porosity fritted glass and washed with 25% hydrochloric acid precooled to 0°C.

The filtrate still contains about 1.5 g. of the oxychloride (or 0.6 g. of ZrO_2) per 100 ml.

VI. A simpler method gives a less complete precipitation. One proceeds as follows.

First 25 g. of $ZrOCl_2 \cdot 8H_2O$ is dissolved in a mixture of 6 ml. of conc. hydrochloric acid and 100 ml. of H_2O. The solution is heated to 70°C and filtered. The filtrate is concentrated to 75 ml. and allowed to cool without stirring. The crystallizing salt is suction-filtered on a fritted glass and washed with a cold 1:1 alcohol–conc. hydrochloric acid mixture, in which the oxychloride is very sparingly soluble. The yield is 10 g. of purified material; an additional 7 g. may be recovered from the mother liquor by further evaporation and crystallization.

SYNONYM:

Zirconyl chloride.

PROPERTIES:

Tetragonal prisms or needles. Deliquescent in moist air, evolves HCl and becomes dull in dry air. Soluble in H_2O (slight hydrolysis) and alcohol. Lower hydrates are formed on heating in a stream of HCl. Liberates HCl on heating in air and the solubility in water is gradually lost; reverts to the oxide on calcination.

Precipitation of an alcoholic solution with ether or acetone yields dizirconyl chloride $Zr_2O_3Cl_2 \cdot 5H_2O$, which is sparingly soluble in water. The same compound deposits when a dilute aqueous solution of zirconyl chloride is allowed to stand for a month.

DropBooks

Hafnium Oxychloride

The preparation and properties of $HfOCl_2 \cdot 8H_2O$ are virtually identical to those of the Zr compound.

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IV. See also H. von Siemens and H. Zander, Wissenschaftl. Veröffentl. Siemens 2, 484 (1922); W. B. Blumenthal, J. Chem. Education 39, 607 (1962).
V. W. Fischer and M. Zumbusch, Z. anorg. allg. Chem. 252, 249 (1944); see also O. Hönigschmid, E. Zintl and F. González, Z. anorg. allg. Chem. 139, 293 (1924) or E. H. Archibald, The Preparation of Pure Inorganic Substances, New York, 1932, p. 187.

VI. W. C. Schumb and E. Pittman in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 121.

Lower Titanium Oxides

TiO, Ti_2O_3

I. The surest preparation of defined lower Ti oxides involves sintering with metallic Ti.

$$\underset{47.9}{Ti} + 3\,\underset{239.7}{TiO_2} = 2\,\underset{287.6}{Ti_2O_3}; \quad \underset{47.9}{Ti} + \underset{79.9}{TiO_2} = 2\,\underset{127.8}{TiO}$$

Filings are prepared from a Ti sheet and ground to pinhead size; a magnet is used to free them from the Fe picked up during the machining operation. The filings are etched with dilute hydrofluoric acid, rinsed with acetone, and rapidly dried. They are mixed with TiO_2 in proper amounts and the mixture is pressed into tablets or rods; these are heated in high vacuum to 1600°C in the arrangement illustrated in Fig. 300.

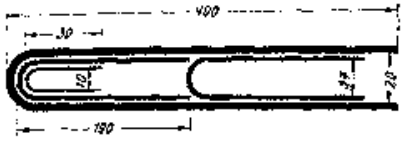

Fig. 300. Synthesis of lower titanium oxides (dimensions in mm.).

Two Tammann crucibles (10 mm. and 14 mm. I.D.), made of sintered clay, are placed one inside the other, and the assembly is placed in a tube (20 mm. I.D. and 400 mm. long) made of the same material and closed at one end. The 14-mm. crucible is loosely covered by the closed end of an identical crucible, as shown. The outer (20 mm. I.D.) tube is connected to a high-vacuum system via a ground joint cemented on with picein. This arrangement of three concentric tubes is needed because the outer corundum tube is not vacuum-tight at the reaction temperature of 1600°C. The gas used for flushing the annular space between the surrounding graphite heater and the inner corundum tube is hydrogen, which diffuses inside. Thus, in new tubes, the inside pressure rises from a satisfactory high vacuum to 1 mm. within 10 minutes at 1600°C; the pressure rises even more rapidly in older tubes. The pump must therefore be left on during the entire heating period. The above arrangement of crucibles prevents the hydrogen from diffusing to the reactants before it can be removed by the vacuum pump.

The mixture is heated at 1600°C for 15 minutes in a Tammann furnace; this is obviously insufficient to bring about complete reaction. The Ti is not completely consumed, but it becomes so brittle that it is readily pulverized in an agate mortar. This fine powder is reheated and the product is then homogeneous.

If Ti powder is used as the starting material, a single but longer heating run is sufficient (1/2 hour at 1600°C).

Materials with a low oxygen content are best subjected to a preliminary homogenization treatment, either by high-frequency heating in high vacuum, or by so-called button-melting in an electric arc, which is familiar in titanium metallurgy.

The above procedure is generally applicable and may be used for the preparation of lower oxides of other elements closely related to titanium, e.g., Zr, Hf, V, Nb, etc.

In many cases it has proved more convenient not to start each run from the metal; in those cases, a larger quantity of the low-oxygen compound is prepared and then used as a stock raw material.

II. Reduction of TiO_2 in a stream of H_2 at 1250°C yields a product of composition $TiO_{1.8}$, at 1430°C and longer reaction times up to $TiO_{1.48}$. At 1000°C, the reduction of TiO_2 in a $TiCl_4$-saturated stream of H_2 also yields a small amount of violet-colored Ti_2O_3, besides the other products.

DroboBooks

III. When TiO_2 is reduced with carbon, the formation of mixed TiO-TiC crystals cannot be entirely prevented. According to Shomate, heating in vacuum at 1400°C for 20 hours yields Ti_2O_3 via the reaction $2\ TiO_2 + C = 2\ Ti_2O_3 + CO$, in agreement with the observations of Junker, who found that significant amounts of carbide are formed only above 1600°C.

PROPERTIES:

TiO: Formula weight 127.80. Golden yellow powder. M.p. 1750°C; d 4.89. Crystal structure: type B1 (NaCl type). The rock salt phase is homogeneous over a wide range of compositions ($TiO_{1.3}$–$TiO_{0.8}$). TiO dissolves in dilute hydrochloric and sulfuric acids with partial oxidation: $Ti^{2+} + H^+ = Ti^{3+} + {}^1/_2\ H_2$.

Ti_2O_3: Formula weight 143.80. Dark violet powder. M.p. ~1900°C; d 4.49. Crystal structure: type $D5_1$.

REFERENCES:

I. P. Ehrlich, Z. Elektrochem. 45, 362 (1939); see also S. Andersson, B. Collén, U. Kuylenstierna and A. Magnéli, Acta Chem. Scand. 11, 1641 (1957).

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Titanium (IV) Oxide

TiO_2

Titanium (IV) oxide crystallizes in three modifications of decreasing stability: rutile, anatase and brookite. Whether the synthesis of brookite has been achieved is still in doubt. Anatase is formed via the hydrolysis of Ti halides at not too high a temperature (600°C) or via low-temperature calcining (~700°C) of precipitated titanic acid. The lattice is stabilized by adsorbed anions, among which the most effective are sulfate and phosphate. Pure TiO_2 calcined at high temperature always yields the rutile lattice.

I. $\underset{189.7}{TiCl_4} \rightarrow \underset{79.9}{TiO_2}$

Very pure TiO_2 is readily prepared by hydrolysis of prepurified and repeatedly distilled $TiCl_4$. The chloride is hydrolyzed in Pyrex vessels cooled in ice and the residual titanic acid is precipitated by addition of ammonia. The mixture is boiled for one hour, filtered and thoroughly washed until free of chloride (if necessary, the precipitate is redissolved in hydrochloric acid before washing, and precipitated with ammonia). The precipitate is dried at 107°C and calcined for one hour at 800°C. The product should be ground to a fine powder, rewashed until free of chloride, and calcined at 1000°C. After calcination, the TiO_2 so prepared is white or light gray. A yellow tinge indicates traces of iron.

Alternate methods:

II. A more readily filtered precipitate is obtained when the precipitation is carried out in the presence of $(NH_4)_2SO_4$. Commercial $TiCl_4$ (900 g.) is slowly added to one liter of distilled water, and the solution is purified by boiling for 10 minutes and removing SiO_2 and any insoluble impurities by filtration. A solution of 1300 g. of $(NH_4)_2SO_4$ in two liters of distilled water acidified with 25 ml. of conc. hydrochloric acid is treated in a similar manner. The two solutions are cooled, combined with stirring, and brought to a boil. The pH is adjusted to 1.0 by addition of

ammonia. At pH<1, the yield is lower, while at pH>1 the Fe content of the product may exceed 0.003%. Further treatment is the same as in (I). The yield is almost quantitative, and a rutile powder with a TiO_2 content exceeding 99.8% is obtained.

III.

$$\underset{240.1}{K_2TiF_6} \rightarrow \underset{79.9}{TiO_2}$$

A solution of K_2TiF_6 (which has been recrystallized several times) in hot water is prepared, and ammonia is added to precipitate the snow-white $TiO_2 \cdot aq$. The precipitate is thoroughly washed, dried and calcined.

IV.

$$\underset{196.0}{TiOSO_4 \cdot 2H_2O} \rightarrow \underset{79.9}{TiO_2}$$

This may be achieved by hydrolysis of titanium sulfate solutions on prolonged boiling. However, this procedure is not recommended since it requires a long time (eight hours) and the resultant precipitates are difficult to filter; precipitation with ammonia at the boiling point is preferred.

V.

$$\underset{189.7}{TiCl_4} + \underset{32.0}{O_2} = \underset{79.9}{TiO_2} + \underset{143.8}{2Cl_2}$$

DropBooks

The following procedure for the preparation of rutile differs fundamentally from the previous methods. Absolutely dry O_2 and $TiCl_4$ vapor are passed for 20 hours through a 20-mm.-I.D. porcelain tube heated to 650–750°C. Colorless to light-yellow, lustrous crystals of rutile are deposited on the white reactor walls. Unreacted $TiCl_4$ is collected in a receiver cooled with ice-salt. Toward the end of the preparation, pure O_2 is passed through the tube, and this stream is continued while the mixture is cooling.

SYNONYM:

Titanium dioxide.

PROPERTIES:

Rutile: type C4, d 4.22; anatase: type C5, d 4.06; brookite: type C21, d 4.13. M.p. 1870°C; thermal dissociation above 1800°C is evident from the appearance of a bluish tinge and a lower melting point.

Amorphous TiO_2 is also insoluble in water and dilute acids. It dissolves slowly in hot conc. H_2SO_4, better in alkali hydrogen

sulfates. The solubility is strongly dependent on the prior thermal treatment.

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IV. Tscheng Da Tschang, Bull. Soc. Chim. France [5] 3, 271 (1936); A. W. Czanderna, A. F. Clifford and J. M. Honig, J. Amer. Chem. Soc. 79, 5407 (1957).
V. H. Rheinboldt and W. Wisfeld, Ber. dtsch. chem. Ges. 67, 375 (1934).

Titanium (IV) Oxide Hydrate

$TiO_2 \cdot n\,H_2O$

I. Compounds belonging to the system TiO_2-H_2O prepared in the usual way (e.g., by precipitation with ammonia from an aqueous solution of K_2TiF_6) may be regarded as composed of TiO_2 and labile H_2O. Part of the water, however, is bound and localized; its amount depends on the method of preparation. Precipitated, hydrated TiO_2 either exhibits an amorphous x-ray pattern or consists of anatase containing adsorbed water; similar lattices are formed by the products of hydrolysis of $Ti(SO_4)_2$ solutions (refluxing for four hours), while hydrolysis of $TiCl_4$ and $Ti(NO_3)_4$ solutions under identical conditions yields rutile.

II. "Orthotitanic acid" H_4TiO_4 or $TiO_2 \cdot 2\,H_2O$ seems to form only under certain definite conditions; using the Wilstätter acetone method at low temperature (0°C), it was possible to prepare a compound of composition $TiO_2 \cdot 2.16H_2O$.

REFERENCES:

For general references, see R. Fricke, Das System TiO_2/H_2O in R. Fricke and G. F. Hüttig, Hydroxyde und Oxydhydrate [Hydroxides and Oxide Hydrates], Leipzig, 1937, p. 211.
I. H. B. Weiser and O. W. Milligan, J. Phys. Chem. 38, 513 (1934); O. Glemser, Z. Elektrochem. 45, 820 (1939); W. Biltz, G. A. Lehrer and O. Rahlfs, Z. anorg. allg. Chem. 244, 281 (1940).
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Peroxotitanic Acid

H_4TiO_5

$$\underset{79.9}{TiO_2} + \underset{34.0}{H_2O_2} + \underset{98.1}{H_2SO_4} + \underset{174.3}{K_2SO_4} + \underset{18.0}{H_2O} = \underset{404.3}{K_2[TiO_2(SO_4)_2] \cdot 3\,H_2O}$$

$$\underset{404.3}{K_2[TiO_2(SO_4)_2] \cdot 3\,H_2O} = \underset{131.9}{Ti(OH)_3 \cdot OOH} + \underset{174.3}{K_2SO_4} + \underset{98.1}{H_2SO_4}$$

According to Schwarz and coworkers, 5 g. of titanic acid hydrate (Merck) is dissolved in 10 ml. of warm conc. H_2SO_4; the solution is diluted to three times its volume with water, cooled to −10°C, placed in a dropping funnel, and added to a solution of 8.6 g. of K_2SO_4 in 15 ml. of 30% H_2O_2. The mixture is cooled to 0°C and allowed to stand in the cold for 1/2 hour; it is then precipitated by addition of about one liter of ice-cold acetone pretreated with H_2O_2 until the appearance of the color of titanium sulfate (alcohol may cause partial reduction of the solution, yielding a product deficient in active oxygen). The precipitate is filtered with suction and washed with ice-cold absolute ether until the filtrate gives a negative reaction with permanganate. The product is dried for several hours in high vacuum at the lowest possible temperature, yielding yellow-red potassium peroxytitanyl sulfate corresponding to the formula $K_2[TiO_2(SO_4)_2] \cdot 3\,H_2O$.

According to K. F. Jahr (see FIAT-Review, Anorganische Chemie, Part III, p. 173) the color is due not to the complex anion, but to the peroxytitanyl cation itself. See also E. Gastinger, Z. anorg. allg. Chem. 275, 331 (1954).

In the preparation of the corresponding zirconium and hafnium salts, which are white but have an analogous structure, the indicated concentrations of the reactants must be very strictly adhered to.

If the complex salt is to be used immediately, purification by thorough washing suffices. The precipitate is dissolved on the filter in ice water and the solution is poured into 10 liters of ice-cold water. Gradual deposition of the pure white precipitate sets in after some time and the precipitation is complete after about 24 hours. The product is purified by filtering, washing with ice water followed by acetone; any adsorbed water is removed by agitating in a shaker flask (three times with 100 ml. of acetone, once with 100 ml. of absolute ether, three times with petroleum ether—all washing operations at 0°C). The remaining petroleum ether is removed by suction and the product is left for about 0.5 hour in a vacuum desiccator which does not contain a drying agent.

The peroxide hydrates of Zr, Hf and Th are prepared by treating a solution of the sulfate (5-10%, based on the oxide content) with an excess of 30% H_2O_2, cooling to −20°C, and precipitating with ammonia below 0°C. The slimy precipitate is removed by

suction from the cooled container with the aid of a filter candle and washed with ice water. The only suitable drying method is the ammonia extraction process described by W. Blitz [Z. Elektrochem. 33, 491 (1927)].

PROPERTIES:

$Ti(OH)_3 \cdot OOH$: Slightly hygroscopic, lemon-yellow powder. Gradually loses its active oxygen at room temperature, with resultant decoloration. Readily soluble without decomposition in dilute H_2SO_4; loses oxygen gradually in water.

REFERENCES:

R. Schwarz and W. Sexauer, Ber. dtsch. chem. Ges. 60, 500 (1927); R. Schwarz and H. Giese, Z. anorg. allg. Chem. 176, 209 (1928); see also R. Schwarz and F. Heinrich, Z. anorg. allg. Chem. 233, 387 (1935).

Zirconium (IV) Oxide

ZrO_2

$$\underset{322.3}{ZrOCl_2 \cdot 8\,H_2O} \rightarrow \underset{123.2}{ZrO_2}; \quad \underset{355.4}{Zr(SO_4)_2 \cdot 4\,H_2O} \rightarrow \underset{123.2}{ZrO_2}$$

Zirconium (IV) oxide is formed when zirconium oxide hydrates or zirconium salts of volatile, oxygen-containing acids (nitrates, oxalates, acetates, etc.) are dehydrated and then calcined.

Usually the oxychloride or sulfate is thermally decomposed between 600 and 1000°C. Either salt must be prepurified by repeated recrystallization. In the case of the sulfate, the thermal decomposition removes the last traces of SO_3 with some difficulty.

The amorphous ZrO_2, which is the first product obtained on heating the oxychloride (300°C), converts at 500°C to the tetragonal modification, which then contains only traces of Cl. Above 600°C the material is monoclinic.

Alternate methods: *a)* For the almost complete decomposition of $ZrOCl_2 \cdot 8H_2O$ with superheated steam (accompanied by evolution of HCl and formation of ZrO_2) see Akhrap-Simonova.

b) The preparation of ZrO_2 by removal of silicon from $ZrSiO_4$ with SiO is described by Zintl et al.

PROPERTIES:

White powder. M.p. 2680°C, b.p. 4300°C; d 5.73. Exists in several modifications. Crystal structure: tetragonal and monoclinic.

The chemical behavior is strongly affected by the nature of the prior thermal treatment. If the compound has been heated to moderate temperatures, it dissolves quite readily in mineral

acids; after heating to high temperatures, it is soluble only in hydrofluoric acid and conc. H_2SO_4; after melting, it is attacked only by hydrofluoric acid. Decomposes readily in alkali hydroxide or carbonate melts, in which it forms acid-soluble zirconates.

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O. Ruff et al. Z. anorg. allg. Chem. 133, 193 (1924); 180, 19 (1929); W. M. Cohn and S. Tolksdorf. Z. phys. Chem. (B) 8, 331 (1930); G. L. Clark and D. H. Reynolds. Ind. Eng. Chem. 29, 711 (1937); L. K. Akhrap-Simonova. Zh. Prikl. Khimii 11, 941 (1938); E. Zintl, W. Bräuning, H. L. Grube, W. Krings and W. Morawietz. Z. anorg. allg. Chem. 245, 1 (1940); A. W. Henderson and K. B. Higbie. J. Amer. Chem. Soc. 76, 5878 (1954).

See also R. Fricke, Das System ZrO_2/H_2O in R. Fricke and G. F. Hüttig, Hydroxyde und Oxydhydrate [Hydroxides and Oxide Hydrates], Leipzig, 1937, p. 219, especially for the formation of oxide hydrates.

Hafnium (IV) Oxide

HfO_2

Hafnium (IV) oxide is prepared by calcination of the hydroxide, oxalate, oxychloride or sulfate at 600–1000°C. The crystallization of the oxide starts at 400°C.

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PROPERTIES:

White powder. M.p. 2780°C; d 9.68. Essentially identical with ZrO_2 in chemical behavior. It probably forms the same types of crystal lattice.

REFERENCE:

G. von Hevesy and V. Berglund. J. Chem. Soc. (London) 125, 2373 (1924).

Thorium (IV) Oxide

ThO_2

I. $\underset{552.2}{Th(NO_3)_4 \cdot 4\,H_2O}$ or $\underset{570.2}{Th(NO_3)_4 \cdot 5\,H_2O}$ or $\underset{518.3}{Th(C_2O_4)_2 \cdot 6\,H_2O} \rightarrow \underset{264.1}{ThO_2}$

Thorium (IV) oxide is obtained by thermal decomposition of thorium oxide hydrate (which is precipitated with ammonia) or salts of oxygen-containing acids. The nitrate and oxalate are especially suitable as starting materials, while the sulfates give off the last traces of SO_3 only with difficulty.

Pure nitrate is placed in a large evaporation dish and is very carefully heated in an electric furnace. The nitrate swells

considerably at 300–400°C and forms a spongy mass, which subsequently collapses and becomes more compact. To prevent the uptake of SiO_2 during calcination of the oxide, the powder obtained on decomposition of the nitrate is placed in a Pt crucible and is then heated for 1–2 hours at 800–850°C.

The oxalate $Th(C_2O_4)_2 \cdot 6H_2O$ gives off its water of crystallization at 300°C and is almost entirely decomposed to the oxide (the weight of the final products is <1% greater than the theoretical) at 450°C.

II. According to Brintzinger and Möllers, active oxide is obtained when thorium chloride, nitrate or sulfate is decomposed with steam at 800°C.

III. For the preparation of oxide hydrates and hydroxides, see the references indicated.

PROPERTIES:

White powder, compact or loose depending on the method of preparation. M.p. 3050°C, b.p. 4400°C; d 9.87. Crystal structure: type C1 (fluorite type). Almost insoluble in acids when calcined at high temperatures, although readily decomposed in bisulfate melts or by evaporation with conc. H_2SO_4. In contrast to TiO_2 and ZrO_2, does not form salts with basic oxides and is therefore insoluble in molten NaOH or Na_2CO_3. The oxide prepared by calcination of the oxalate at 500°C may be dissolved by peptization with dilute hydrochloric acid.

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Titanium, Zirconium and Thorium Sulfides

TiS_3, TiS_2, $TiS_{<2}$

TiS_3, TiS_2

I.

$$\underset{189.7}{TiCl_4} + 2\,\underset{68.2}{H_2S} = \underset{112.0}{TiS_2} + 4\,\underset{145.9}{HCl}$$

$$\underset{112.0}{TiS_2} + \underset{32.1}{S} = \underset{144.1}{TiS_3}$$

Titanium (IV) sulfide TiS_2 is usually prepared by the reaction of a gaseous mixture of $TiCl_4$ and H_2S in a red-hot tube. A

chlorine-free product cannot be obtained without an aftertreatment with S in a pressure tube at 600°C. The yield is also unsatisfactory (30–40%, based on the $TiCl_4$); however, the yield may be increased by repeated passage of the unreacted $TiCl_4$ from the receivers.

The reaction is carried out in the apparatus shown in Fig. 301; it consists of a Pyrex combustion tube fused at both ends to 100-ml. round-bottom flasks. Flask *a* is filled with 50 g. of freshly distilled $TiCl_4$ and is then sealed off at *c*; *b* is a receiver for unreacted $TiCl_4$, and is cooled with ice-salt. A Stock receiver cooled with Dry Ice and containing about 25 ml. of liquid H_2S is connected to the system at *d* via a small wash bottle filled with glycerol (this is the bubble counter) and two $CaCl_2$ drying tubes. A fast stream of H_2S, generated by gradual removal of the coolant, is passed through the apparatus while the combustion tube is heated to 480–540°C. The $TiCl_4$ in *a* is then heated almost to the boiling point and held at this temperature with a small flame. The $TiCl_4$–H_2S gas mixture reacts in the tube to form HCl and TiS_2; the latter settles on the tube wall. After all the $TiCl_4$ is distilled from *a*, the system is flushed for a short time with H_2 or CO_2, the H_2S line is reconnected at *e*, and the unreacted $TiCl_4$ condensed in *b* is passed again through the tube, this time into *a*. After the $TiCl_4$ has been used up (3–5 hours), the TiS_2 produced is treated for two hours at the same temperature in a slow stream of H_2S to remove most of the chloride still adhering to the product. The material is allowed to cool in a stream of H_2 or CO_2, the tube is broken at both ends, and the dark brass-yellow TiS_2, which crystallizes as leaflets of mosaic gold color, is collected. The yield is about 10 g.

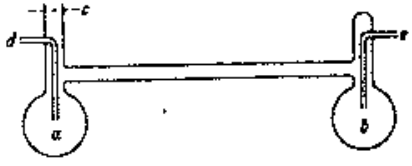

Fig. 301. Preparation of titanium disulfide.

Complete removal of the chloride can be effected only by repeated heating of the product with excess S in a pressure tube. Thus, 4 g. of crude TiS_2 and 3 g. of S are placed in a bomb tube of Vycor or similar glass. The sulfur should be completely free of carbon compounds [von Wartenberg method: Z. anorg. allg. Chem. 251, 166 (1943); this consists of vacuum distillation, followed by 48-hour heating at 200°C in vacuum or under N_2, followed by another vacuum distillation]. The bomb

tube with the TiS_2 and S is sealed in high vacuum and heated for three days at 600°C. The tube is opened and the volatile components are removed in a heated vacuum desiccator (drying pistol) at 100–150°C. The product, which still contains some chloride, is again heated with additional S to about 600°C for two days, and the volatile components are again removed in vacuum. The intermediate product then consists of graphitelike trisulfide and unreacted S. The free sulfur may be removed by vacuum distillation at 400°C; the residual TiS_3 undergoes thermal decomposition at temperatures above 500°C, yielding pure TiS_2.

II.

Ti	+ 2S	= TiS_2;	Ti	+ 3S	=	TiS_3
47.9	64.1	112.0	47.9	96.2		144.1

Sulfides of any desired composition may be obtained by synthesis from the elements, which is a generally applicable method. This is also the simplest way to prepare chlorine-free products. The starting material consists either of Ti filings made by grinding Ti strips (for the preparation of the strips, see the directions for the lower titanium oxides, p. 1214) or simply Ti powder (which, however, usually has a lower metal content). First 1.5 g. of Ti and 4 g. of S, in a thick-wall Vycor tube, are carefully degassed in high vacuum. The tube is then sealed and heated at 650°C for four days. Metal particles still present in the product are ground separately, added to the sulfide product (total about 3 g.) together with 1.7 g. of S, and again heated in a pressure tube for two days at 600°C. The free sulfur is distilled off at 400°C; the higher sulfides are, if desired, decomposed thermally above 500°C, yielding TiS_2 and TiS_3, as in method I.

PROPERTIES:

TiS_2: Formula weight 112.02. Brass-yellow flakes with a metallic luster, d 3.22. Crystal structure: type C6.

Stable in air at normal temperatures; forms TiO_2 on heating. Decomposes in nitric acid and hot conc. H_2SO_4, releasing S; dissolves in boiling aqueous sodium and potassium hydroxides, forming alkali titanates and alkali sulfides.

TiS_3: Formula weight 144.08. Graphitelike substance. d 3.22. Except for its insolubility in boiling NaOH, it is similar to TiS_2 in all chemical properties.

$TiS_{<2}$

Lower Ti sulfides may be prepared by synthesis from the elements, by treatment of Ti metal with TiS_2, or by reduction of TiS_2 with H_2.

SYNTHESES STARTING FROM TITANIUM METAL

The procedure is identical to that of method II; in the first stage the S is bound to the Ti, and the resultant product is subsequently homogenized at high temperature. As long as the presence of sulfur is still a possibility, the temperature is raised very slowly, so that it may require as long as two days to reach 800°C in the case of S-rich compounds and 1000°C for S-poor compounds. The above temperatures are then maintained for 2-3 additional days, after which the product is tested for homogeneity by x-ray analysis.

The reaction is carried out in a quartz tube, which undergoes only slight devitrification but no further changes. Titanium metal itself begins to react with quartz at about 850°C. To exclude entirely the possibility of reaction of the titanium with the quartz in the case of the subsulfides ($TiS_{<1}$), the reaction mixture is placed in small ceramic or sintered clay crucibles (8-mm. diameter, 30 mm. long) which are then inserted in suitable quartz tubes and the tubes sealed off. This complication usually results in the necessity of using tubes of lesser wall thickness; hence, greater care must be exercised during heating.

As in other cases where tubes are to be heated to temperatures as high as 800°C, protection against explosion is recommended; this is provided by wrapping the tube in asbestos paper and inserting it into a small cage made of several layers of Ni or Cu wire mesh.

When quartz tubes are cut open with an emery wheel (1 mm. thick), it is not always possible to prevent quartz splinters from getting into the product. If the material is not a mass with a solid, glossy surface affording easy visual separation, the embedded quartz particles should always be removed by shaking with bromoform followed by centrifugation.

REDUCTION OF TiS_2 WITH H_2

This method permits carrying the reduction as far as the monosulfide stage, provided high temperatures are used. Since all small amounts of Cl present are removed during the reduction, the crude TiS_2 produced by method I can be used as such without further purification. The reaction is carried out in an unglazed porcelain tube, with the boat containing the material placed in the center; a stream of carefully dried H_2 (freed of O_2 by contact with Pd) is passed over the boat. Two to three hours suffice for the reduction; the duration of the run depends on the quantity of material and the hydrogen flow rate. The temperature to which the tube is heated is a deciding factor for the degree of reduction (500°C → $TiS_{1.50}$, 900°C → $TiS_{1.25}$, 1200°C → $TiS_{1.1}$).

PROPERTIES:

Air stable, colored substances ($TiS_{1.5}$: black; $TiS_{1.13}$: violet; $TiS_{1.0}$: brown; $TiS_{0.5}$: gray). With decreasing sulfur content, the susceptibility to hydrochloric acid attack increases and that by acidic oxidation agents decreases. In contrast to TiS_2, the lower sulfides are unaffected by sodium hydroxide. The sesquisulfide phase has a wide range of compositions ($TiS_{1.58}$–$TiS_{1.13}$).

REFERENCES:

W. Biltz and P. Ehrlich. Z. anorg. allg. Chem. 234, 97 (1937); see also H. Hahn and B. Harder. Ibid. 288, 241 (1956) (also contains information on growing of single crystals).

Zirconium Sulfides

Zirconium sulfides can be prepared by exactly parallel methods, i.e., reaction of $ZrCl_4$ with H_2S or synthesis from the elements. Orange-red ZrS_3 may be thermally decomposed to brown ZrS_2 at 800°C. The lower zirconium sulfides include, in addition to the sesquisulfide and subsulfide phases, an additional compound $ZrS_{0.75}$.

REFERENCE:

E. F. Strotzer and W. Biltz. Z. anorg. allg. Chem. 242, 249 (1939).

Thorium Sulfides

Synthesis from the elements under pressure yields a deep red polysulfide Th_3S_4, lilac brown ThS_2, a sesquisulfide, and a subsulfide $ThS_{0.75}$.

REFERENCE:

E. F. Strotzer. Z. anorg. allg. Chem. 247, 415 (1941).

Titanium (III) Sulfate

$$Ti_2(SO_4)_3$$

$$\underset{379.5}{2\,TiCl_4} \rightarrow \underset{384.0}{Ti_2(SO_4)_3}$$

Titanium tetrachloride (100 g.) is carefully decomposed with approximately four times its volume of H_2O. The solution is cooled

and treated with dilute ammonia to precipitate $TiO_2 \cdot aq.$, which is suction-filtered, thoroughly washed with water, and dissolved (vigorous shaking) in 70 ml. of conc. H_2SO_4. The solution is diluted with water to one liter, the precipitation with ammonia is repeated, and the resultant deposit is reprecipitated two additional times. The $TiO_2 \cdot aq.$ obtained (about 480 g.) is carefully dissolved in 100 ml. of conc. H_2SO_4, yielding a total liquid volume of about 500 ml.; this is suction-filtered through glass and treated with 300 ml. of conc. H_2SO_4, yielding about 400 ml. of a solution of Ti (IV) sulfate. This solution is reduced to Ti (III) sulfate by the following electrolytic method.

A low vertical cylinder closed off with a rubber stopper serves as the electrolysis vessel and contains the sulfate solution. The anode is a piece of Pt sheet immersed in a clay cell filled with 20% H_2SO_4. The cell is partially immersed in the Ti (IV) sulfate solution and is surrounded by four amalgamated lead strips, also immersed in the solution. The stopper on the outer electrolysis vessel has holes for the clay cell and for the inlet and outlet gas tubes. The electrolysis is carried out in a constant stream of CO_2 and with efficient water cooling. The current density is 0.06 amp./cm.^{2} at 24 v. for the first six hours, then 0.33 amp./cm.^{2} at the same voltage for an additional six hours. This reduces all the Ti (IV) sulfate to Ti (III) sulfate; the latter precipitates as an H_2SO_4-containing hydrate (fine, pale light violet crystals).

To obtain the anhydrous Ti (III) sulfate, the product is suction-filtered in a stream of CO_2, washed with 50% H_2SO_4, and placed (in the absence of air) in a round-bottom flask fitted with a ground joint and filled with CO_2. Then 300 ml. of dilute sulfuric acid (20% v./v. H_2SO_4) is added; the flask is stoppered with a ground stopper fitted with inlet and outlet gas tubes and an opening for the insertion of a thermometer; it is heated in a stream of CO_2 until the precipitate dissolves. Using gas pressure, the liquid is forced into a filtration apparatus (see Part I, p. 74) and filtered under CO_2 through a tubular fritted glass filter fitted with appropriate ground joints. The receiver with the filtrate is in turn closed off with a stopper fitted with a thermometer and gas tubes; CO_2 is passed through, and the temperature is slowly raised by means of an oil bath. This concentrates the liquid to about half its volume. At this point a violet precipitate begins to form; on further heating, this turns to blue and finally, at 190–200°C, to green. The temperature is maintained at 190°C for three hours and is then raised to 210–220°C for 10 minutes. Heating to higher temperatures results in evolution of SO_2 and oxidation of the Ti (III) sulfate. The material is allowed to cool in a stream of CO_2; it should remain green. If it assumes a blue color, the heating procedure must be repeated. The green precipitate is filtered under CO_2 using the filtration apparatus; the contaminating Ti (IV) sulfate

is removed by washing with conc. H_2SO_4, followed by glacial acetic acid, anhydrous methanol and ether. The tubular fritted glass filter is removed from the filtration system, covered with a ground cap fitted with a stopcock, and placed horizontally in a short tubular electric furnace; the material is then dried for four hours at 140°C in a constant stream of pure N_2.

PROPERTIES:

Green crystalline powder. Insoluble in water, alcohol and conc. H_2SO_4; soluble in dilute H_2SO_4 and in hydrochloric acid, yielding a violet solution.

REFERENCES:

O. Schmitz-Dumont, P. Simons and G. Broja, Z. anorg. Chem. 258, 307 (1949); W. J. de Haas and B. H. Schultz, Physica [2] 6, 481 (1939); A. Stähler and H. Wirthwein, Ber. dtsch. chem. Ges. 38, 2619 (1905).

Titanoxy Sulfate

$TiOSO_4$

This compound is produced on evaporation of TiO_2 or TiO_2 · aq. with conc. H_2SO_4; the dihydrate is obtained under the same conditions but with 70% H_2SO_4. The material, which is extremely hygroscopic and readily splits off SO_3, can also be prepared as a white precipitate by dropwise addition of a solution of SO_3 in SO_2Cl_2 to a solution of $TiCl_4$ in SO_2Cl_2, followed by refluxing [E. Hayek and W. Engelbrecht, Monatsh. Chemie 80, 640 (1949)].

Iron-free titanoxy sulfate is usually not available commercially. When available, it is not completely water soluble. The following procedures are therefore recommended for the preparation of the pure compound.

I. $TiOSO_4$

$$\underset{189.7}{TiCl_4} + \underset{98.1}{H_2SO_4} + \underset{18.0}{H_2O} = \underset{160.0}{TiOSO_4} + \underset{145.8}{4\,HCl}$$

Pure, multiple-distilled $TiCl_4$ is added in drops (vigorous stirring) to the stoichiometric quantity of 50% H_2SO_4. The precipitate formed after each addition should dissolve completely before the next portion of $TiCl_4$ is added. After the addition of about 3/4 of the $TiCl_4$, the liquid turns into a viscous, yellowish solution. It

is diluted with 1/5 its volume of water, and the dropwise addition of $TiCl_4$ is completed.

The resultant solution, which is still highly concentrated in HCl, is evaporated to dryness on a water bath. The residue is pulverized, dried and freed of HCl by heating for several days at 80–100°C in a drying pistol at a pressure of a few mm.

The sulfate obtained in this manner (TiO_2:SO_3 = 1:1.07) is colorless and free of HCl. It is hygroscopic and soluble in water, yielding a clear solution.

Gelatinous or resinous precipitates may appear during the evaporation of the HCl-containing, highly viscous and slightly yellow solutions; the same phenomenon may occur during the vacuum concentration operation. Addition of alcohol or acetone to the concentrated solutions leads to the formation of fibrous precipitates.

II. $TiOSO_4 \cdot 2\,H_2O$

$$\underset{189.7}{TiCl_4} + \underset{36.0}{2\,H_2O} = \underset{79.9}{TiO_2} + \underset{145.8}{4\,HCl}$$

$$\underset{79.9}{TiO_2} + \underset{98.1}{H_2SO_4} + \underset{18.0}{H_2O} = \underset{196.0}{TiOSO_4 \cdot 2\,H_2O}$$

DropBooks

A solution of 40 ml. (63 g.) of freshly distilled $TiCl_4$ (b.p. 134–138°C) in 130 ml. of water is prepared. Most of this solution is then reduced to a slight extent by means of Zn rods or, better, by electrolysis (light-brown color), while 10 ml. kept separately is reduced to the trivalent titanium ion (deep violet color). The reduction is intended to ensure that all the iron is present in the form of Fe^{2+}, to avoid hydrolysis and coprecipitation of Fe^{3+} with the Ti. The reaction is carried out in dilute oxalic acid.

The violet chloride solution is slowly added in drops to a boiling solution of 1 g. of oxalic acid in one liter of water; then the brown chloride solution is added in the same way. The mixture should be maintained at the boiling point for a total of four hours, the volume being kept constant by occasional addition of water. The conditions of precipitation must be closely adhered to, to prevent coprecipitation of unfilterable metatitanic acid. The precipitate is filtered through a large Büchner funnel, washed free of Cl with boiling water and dried by suction. It is then treated with 35 ml. of conc. H_2SO_4 in a beaker. The mixture is gently boiled until precipitation begins. After cooling and addition of 120 ml. of water, the mixture is allowed to stand (with occasional stirring) for several days and, if necessary, is filtered. It is then evaporated, precipitating crystals of $TiOSO_4 \cdot H_2O$.

III. $TiOSO_4$ solutions

$$\underset{79.9}{TiO_2} + 2\,\underset{256.3}{KHC_2O_4} + \underset{18.0}{H_2O} = \underset{354.2}{K_2TiO(C_2O_4)_2 \cdot 2\,H_2O}$$

$$\underset{354.2}{K_2TiO(C_2O_4)_2 \cdot 2\,H_2O} + \underset{196.2}{2\,H_2SO_4} =$$

$$\underset{174.3}{K_2SO_4} + \underset{160.0}{TiOSO_4} + \underset{56.0}{2\,CO} + \underset{88.0}{2\,CO_2} + \underset{72.1}{4\,H_2O}$$

Iron-free titanium sulfate solutions, used as analytical standards, are readily prepared by repeated recrystallization of $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ followed by treatment with conc. H_2SO_4.

A concentrated solution of KHC_2O_4 is saturated at the boiling point with freshly precipitated $TiO_2 \cdot aq.$; the mixture is concentrated, whereupon white needles precipitate out. The double salt is dissolved with heating in an approximately equal weight of water. The solution is filtered and the salt is recrystallized in about 80–90% yield by cooling with ice and stirring. The iron content is reduced in the process from 0.061% to 0.004%, and no further iron can be detected after another repetition of the crystallization. The analytically pure salt has a composition corresponding to $K_2TiO(C_2O_4)_2 \cdot 2H_2O$.

To prepare one liter of an approximately 0.1N Ti sulfate solution, 38 g. of the double oxalate is thoroughly mixed with 32 g. of pure $(NH_4)_2SO_4$ (iron-free!) and placed in a 750-ml. Kjeldahl flask. The addition of $(NH_4)_2SO_4$ facilitates the reaction. Then 80 ml. of pure conc. H_2SO_4 is added. The flask is heated carefully with a small flame until cessation of foaming, and the solution is then boiled on a strong flame to decompose the oxalate. The solution is cooled, whereupon it becomes sirupy; it is carefully added, with vigorous stirring, to 500 ml. of distilled water and is then diluted to one liter. If precipitation occurs after standing overnight, the solution is filtered. The solution should give a negative test for oxalate upon addition of 1 drop of 0.1N $KMnO_4$ to 50 ml. of the liquid.

IV. *Alternate method:* Pure $TiOSO_4 \cdot 2H_2O$ precipitates in the form of long crystal needles from a solution of $TiO_2 \cdot aq.$ in 60–70% H_2SO_4 in which the ratio $TiO_2 : H_2SO_4 = 1:3$ to $1:7$. At higher concentrations of acid, the precipitate is powdery and contains less H_2O.

SYNONYM:

Titanyl sulfate.

PROPERTIES:

Anhydrous: highly hygroscopic; dissolves slowly in water to give a clear solution. Dihydrate: readily soluble. Decomposes in hot H_2O with precipitation of $TiO_2 \cdot aq$.

REFERENCES:

I. Private communication from K. F. Jahr, Berlin.
II. A. W. Hixson and W. W. Plechner, Ind. Eng. Chem. 25, 262 (1933).
III. R. Rosemann and W. M. Thornton, J. Amer. Chem. Soc. 57, 328 (1935); see also C. Péchard, Comptes Rendus Hebd. Séances Acad. Sci. 116, 1513 (1893); A. Rosenheim and O. Schütte, Z. anorg. Chem. 26, 239 (1901).
IV. A. V. Pamfilov and T. A. Chudyakova, Zh. Obschey Khimii 19, 1443 (1949).

Zirconium Sulfates

$Zr(SO_4)_2 \cdot 4H_2O$

Hauser and more recently Falinski have made a thorough study of the system $ZrO_2/SO_3/H_2O$ as a function of the SO_3 concentration. It was found that the tetrahydrate is formed on addition of $ZrOCl_2 \cdot 8H_2O$ to a sulfuric acid containing less than 64% SO_3 (d 1.714). The tetrahydrate solubility is then 2%. The minimum solubility (0.3%) corresponds to 50% SO_3 in the acid (d 1.517).

If the SO_3 content exceeds 64%, acid sulfates precipitate: $Zr(SO_4)_2 \cdot H_2SO_4 \cdot 2H_2O$ at an SO_3 concentration of 64–72%, and $Zr(SO_4)_2 \cdot H_2SO_4 \cdot H_2O$ at 72–79% SO_3.

PROPERTIES:

Formula weight 355.41. Orthorhombic crystals. The basic salt precipitates slowly from neutral, saturated solution, rapidly from dilute solution or above 40°C.

In sulfuric acid solution, the Zr migrates to the anode instead of to the cathode; therefore, the tetrahydrate may actually be present in the form of a disulfatooxozirconic acid ($H_2[OZr(SO_4)_2] \cdot 3H_2O$).

$Zr(SO_4)_2$

The anhydrous salt is obtained by evaporation of the tetrahydrate or Zr oxychloride with conc. H_2SO_4.

Thus, 100 g. of $ZrOCl_2 \cdot 8H_2O$ is mixed with 50 g. of conc. H_2SO_4 and, after termination of the gas evolution, carefully evaporated with stirring on a sand bath. The dihydrate of the sulfate crystallizes out as an intermediate in the process, but decomposes on further heating, giving off additional H_2O. The excess H_2SO_4 is completely evaporated by heating to 350–380°C. The product is allowed to cool in a desiccator.

PROPERTIES:

Formula weight 283.35. Microcrystalline powder. Very hygroscopic; in air, forms an unstable solution from which the normal tetrahydrate crystallizes after some time. The anhydride dissolves more rapidly in a small than in a large amount of water, since the temperature rise produced by the heat of hydration sharply accelerates the solution process.

REFERENCES:

O. Hauser, Z. anorg. allg. Chem. 106, 1 (1919); M. Falinski, Ann. Chimie 16, 237 (1941).

Purification of Zr salts via the tetrahydrate

One volume of conc. H_2SO_4 is added to two volumes of a moderately conc. aqueous solution of Zr sulfate or chloride; the thick, white, crystalline precipitate of $Zr(SO_4)_2 \cdot 4H_2O$ is readily filtered with suction on fritted glass of medium porosity. Since 1 g. of the salt dissolves in 1 ml. of H_2O, the Zr sulfate is easily dissolved; it is reprecipitated by addition of conc. H_2SO_4. The iron is efficiently removed during the recrystallization provided the solution contains about 10% HCl. After each precipitation, the solid is washed several times with a solution made up of 15 parts by volume of H_2O, eight parts of conc. H_2SO_4 and one part of conc. hydrochloric acid, followed by three washings with acetone. Alcohol should not be used for washing, since it forms complexes during the further precipitations.

Thus, 1135 g. of commercial $ZrCl_4$ [equivalent to 1731 g. of $Zr(SO_4)_2 \cdot 4H_2O$] was dissolved in 1800 ml. of H_2O and 250 ml. of conc. HCl; then 100 ml. of conc. H_2SO_4 was added, precipitating 1640 g. (94%) of $Zr(SO_4)_2 \cdot 4H_2O$; five additional crystallizations of this product (under identical conditions) finally give 1212 g. of pure tetrahydrate. The following table shows the degree of purification achieved:

Starting material	>0.1% Fe	<0.1% Mg, Si	<0.01% Ag, Al, Ba, Ti	<0.001% Ca, Cu, Mn	<0.0001% —	<0.00001% —
4 × recrystallized	—	—	—	Ca, Mg, Na, Si	Ag	Fe, Cu

A residual Fe content up to 0.01% may be removed by mere recrystallization, without the addition of HCl. The Hf content of 2.7% remains unchanged.

REFERENCE:

W. S. Clabaugh and R. Gilchrist. J. Amer. Chem. Soc. 74, 2104 (1952).

Titanium, Zirconium and Hafnium Nitrides

TiN, ZrN, HfN

Titanium Nitride

A number of procedures are available. The simplest is the industrial process starting from $TiO_2 + C + N_2$ described in method I. If metallic Ti is available, synthesis from the elements (method II) is recommended. Very pure nitride in rod or wire form, especially well suited for physical measurements, is obtained by vapor deposition (method III). An additional method of lesser importance consists of the reaction between $TiCl_4$ and NH_3 (method IV).

DropBooks

I.
$$\underset{159.8}{2\,TiO_2} + \underset{48.0}{4\,C} + \underset{28.0}{N_2} = \underset{123.8}{2\,TiN} + \underset{112.0}{4\,CO}$$

The industrial process does not yield a pure product. Acetylene-derived carbon black is degassed at 1200°C, mixed with TiO_2 (mole ratio 1:2), and the mixture placed in a silicon carbide or molybdenum boat; it is calcined for three hours at 1250°C in a stream of N_2. The product contains 98% nitride; the remainder is lower Ti oxides.

II.
$$\underset{95.8}{2\,Ti} + \underset{28.0}{N_2} = \underset{123.8}{2\,TiN}$$

In the first stage of this preparation, the ductile metal absorbs small quantities of N_2 and thus becomes brittle; it can then be pulverized for further treatment with nitrogen.

TREATMENT WITH NITROGEN

Titanium filings ground to pinhead size and treated as described in the directions for the preparation of TiO (p. 1214) are placed in a silicon carbide or molybdenum boat and heated to 1200°C

for 2-3 hours. The operation is carried out in a hard porcelain tube in a stream of pure, dry N_2. The product has the approximate composition $TiN_{0.95}$; it is finely ground and subjected to a second nitrogenation. The desired composition is attained in two to three repetitions of the procedure. The quality of the product is adversely and decisively affected by the presence of the slightest traces of O_2 or H_2O during heating.

PRESINTERING

The products prepared in the above manner are ground as finely as possible and compressed under 2000 kg./cm.^{2} into rods 3 × 40 or 5 × 40 mm. Successful molding usually requires the addition of 2-5% of metal powder. The rods are embedded in nitride powder (to prevent formation of an oxide coating) and presintered in a small tubular tungsten furnace (cf. Part I, p. 40) at about 2300°C in a stream of N_2; the small amount of free metal is converted to nitride in the process. Since the reaction is usually accompanied by considerable shrinkage of the rods and concomitant appearance of porosity, the material must be repulverized, remolded and resintered. This procedure is repeated two to four times, until the presintered rods exhibit some constancy of density.

HIGH-TEMPERATURE SINTERING

When the rods have attained sufficient strength and density in the presintering process, they are fastened with clamps in preparation for direct electrical heating. The operation is carried out in technical-grade Ar containing 12-15% N_2; the equipment used has been described by C. Agte and H. Alterthum, Z. techn. Phys. 11, 182 (1930).

The nitrides are heated to just below their melting points. At these extreme temperatures, all impurities (except some oxides and the carbides) possess higher vapor pressures than the nitrides and therefore evaporate. However, the oxides, even though their melting points are lower, are difficult to remove. The carbides, with higher melting points than the nitrides, remain unchanged.

III. $$\underset{379.4}{2\,TiCl_4} + \underset{28.0}{N_2} + \underset{8.1}{4\,H_2} = \underset{123.8}{2\,TiN} + \underset{291.7}{8\,HCl}$$

The technique used in the vapor deposition process is the same as that described for the preparation of the metals (Ti, Zr and Hf) from the gas phase, except that the gas used here is a $TiCl_4$-saturated mixture of H_2+N_2 (the reaction at the glowing wire is less successful with N_2 alone).

A gasometer is filled with a mixture of equal volumes of H_2 and N_2. The gas bubbles through a 36°C wash bottle filled with

$TiCl_4$ (p of $TiCl_4$ = 17 mm.). The gas flow rate is of no importance, except that it must be low enough to achieve saturation. The optimum reaction pressure is about 30–40 mm., measured with a manometer whose mercury surface is protected by a thin film of butyl phthalate.

The reactor is a round-bottom Pyrex flask with inlet and outlet tubes for the gas fused on the sides. The arc-shaped glow wire (about 8–10 cm. long) is welded to two thick tungsten electrodes; these are sealed into a ground joint inserted through the bottom of the flask. The 0.2-mm. glow wire may be either W or Ta. Wires of Ta can be directly welded to the W rods, whereas the W wires have to be connected via a short Ni bridgepiece.

In the course of the reaction, the glow wire is heated to about 1450°C; since the deposited TiN is itself a good electrical conductor, the current must be raised from 10 to about 22 amp. within the first 40 minutes. One serious disadvantage of the process is the fact that the temperature cannot be measured with an optical pyrometer because $TiCl_3$, one of the products of the fast decomposition of $TiCl_4$, soon coats the flask walls. One must resort, therefore, to indirect estimation of the temperature by measuring it in a blank run with gases containing no $TiCl_4$. The nitride deposits as a fine crystalline coating of copper to gold luster.

Alternate methods:

IV. $TiCl_4 + NH_3 \rightarrow TiN$

189.7 17.0 61.9

DropBooks

As we have indicated before, this process is less desirable. Chlorine-containing TiN is formed (in poor yield) on the walls of a porcelain tube in which a gaseous mixture of $TiCl_4$ and NH_3 is thermally decomposed at 800°C. The same result is obtained when the solid compound $TiCl_4 \cdot 4NH_3$ is placed at the front end of the tube, evaporated in a stream of NH_3, and allowed to react at 800°C.

The $TiCl_4$ ammoniate is prepared by distilling the $TiCl_4$ into a bomb tube and covering the liquid with excess NH_3 at −60°C; the pale yellow compound is formed after shaking the sealed tube for 12 hours at room temperature.

The "crude nitride" formed at 800°C is heated in a hard porcelain tube at 1500°C for six hours in a stream of NH_3 to obtain a Cl-free product of the composition TiN.

PROPERTIES:

Bronze-colored powder. M.p. 2950°C; d 5.21. Somewhat dissociated at the melting point. Crystal structure: type B1 (NaCl type). This structure holds for a wide range of compositions ($TiN_{1.0}$–$TiN_{0.4}$). Very good electrical conductor.

Insoluble in HCl, HNO_3 and H_2SO_4, even on boiling; dissolves rapidly in hot aqua regia. Evolves NH_3 on boiling in potassium hydroxide and on heating in soda lime.

Zirconium Nitride, Hafnium Nitride

These compounds are prepared by the same methods as above.

I. The experimental arrangement is the same as for TiN, except that the reaction temperature is higher (about 1300°C). Since Mo begins to form a carbide at this temperature, the equipment must be made of tungsten. The products are only about 90% pure; the remainder is mainly the oxide.

II. Yellowish-brown ZrN (m.p. 2980°C) is synthesized from the elements by heating the latter for two hours at 1200°C. The corresponding temperature for HfN is 1400-1500°C.

III. The vapor deposition method: If H_2 (or $H_2 + N_2$, or NH_3) is the carrier gas for $ZrCl_4$ (or $HfCl_4$) the required wire temperatures are 2000-2400°C. With pure N_2, the temperature must be 2900°C and the rate of deposition is considerably slower.

Nitridation of Zr wire by heating in pure N_2 produces ZrN at very low rates and in a very loose and brittle form, even if the temperature is almost at the melting point of the metal (1860°C).

REFERENCES:

General: C. Agte and K. Moers, Z. anorg. allg. Chem. 198, 233 (1931).

I. E. Friederich and L. Sittig, Z. anorg. allg. Chem. 143, 293 (1925).

II. P. Ehrlich, Z. anorg. Chem. 259, 1 (1949); G. L. Humphrey, J. Amer. Chem. Soc. 75, 2806 (1953).

III. A. E. van Arkel and J. H. deBoer, Z. anorg. allg. Chem. 148, 345 (1925); F. H. Pollard and P. Woodward, J. Chem. Soc. (London) 1948, 1709; Trans. Faraday Soc. 46, 190 (1950); F. H. Pollard and G. W. A. Fowles, J. Chem. Soc. (London) 1952, 2444.

IV. A. Brager, Acta Physiochim. URSS 11, 617 (1939); see also O. Ruff and F. Eisner, Ber. dtsch. chem. Ges. 41, 2250 (1908); 42, 900 (1909).

Thorium Nitride

Th_3N_4

I.

$$\underset{696.4}{3\,Th} + \underset{56.0}{2\,N_2} = \underset{752.4}{Th_3N_4}$$

Thorium nitride is usually prepared by heating Th filings in a stream of dry, pure N_2. The reaction is complete in three

hours at 800°C. The presence of oxide in the metal is detrimental (products lower in N are formed).

II. *Alternate methods:*

a) $$3\,ThCl_4 + 2\,N_2 + 6\,H_2 = Th_3N_4 + 12\,HCl$$
$$\underset{}{1122} \quad \underset{}{56} \quad \underset{}{12} \quad \underset{}{752} \quad \underset{}{438}$$

Since Th_3N_4 is not an electrical conductor, the method of vapor deposition (used in the preparation of pure TiN and ZrN) gives poorer results. Thus, solid $ThCl_4$ is made to react with $N_2 + H_2$ in a flask maintained at 800°C. The tungsten glow wire is at < 1000°C. The yield is poor.

b) $$3\,ThO_2 + 6\,C + 2\,N_2 = Th_3N_4 + 6\,CO$$
$$\underset{}{793} \quad \underset{}{72} \quad \underset{}{56} \quad \underset{}{752} \quad \underset{}{168}$$

A sintered tungsten rod containing ThO_2 + graphite is calcined above 2000°C in a N_2-containing atmosphere; black Th_3N_4 crystals and lighter, oxide-containing products are formed.

PROPERTIES:

Dark-brown, almost black powder. Stable in dry air; readily soluble in acids.

DropBooks

REFERENCES:

I. B. Neumann, C. Kröger and H. Haebler. Z. anorg. allg. Chem. 207, 145 (1932).
II. W. Düsing and M. Hüniger. Techn. Wissenschaftl. Abhdlg. Osram 2, 357 (1931).

Titanium Tetranitrate

$Ti(NO_3)_4$

I. $$TiCl_4 + 4\,N_2O_5 = Ti(NO_3)_4 + 4\,NO_2Cl$$
$$\underset{}{189.7} \quad \underset{}{432.0} \quad \underset{}{296.0} \quad \underset{}{325.7}$$

A solution of 3 ml. (5.1 g.) of $TiCl_4$ in 10 ml. of CCl_4 is cooled with Dry Ice in a two-neck flask provided with a dropping funnel and a reflux condenser which is protected with a P_2O_5 tube. A solution of 11.6 g. of N_2O_5 in 25 ml. of CCl_4 is then added dropwise. A yellow, flocculent precipitate forms as soon as the CCl_4 melts (−23°C), that is, after removal of the coolant. As the temperature

rises from −23°C to room temperature, the precipitate dissolves with evolution of a gas. If too violent, the bubbling may be slowed down by cooling. Solution of the last fraction of the precipitate is accelerated by mild heating. The volatile components (NO_2Cl and CCl_4) are removed by vacuum distillation, leaving a residue of the white $Ti(NO_3)_4$, which may be purified by sublimation in high vacuum at 50°C. Part of the product decomposes in the process into N_2O_5 and nonvolatile $TiO(NO_3)_2$.

II. $$\underset{189.7}{TiCl_4} + 4\,\underset{389.9}{ClNO_3} = \underset{296.0}{Ti(NO_3)_4} + 4\,\underset{283.6}{Cl_2}$$

A large excess of $ClNO_3$ is condensed at liquid nitrogen temperature onto the surface of 2-3 ml. of $TiCl_4$, frozen in a cold trap at high vacuum. The trap is connected to a surge vessel and the temperature is raised to −80°C. The reaction, which is accompanied by evolution of chlorine, is complete after a few hours. The volatile components (Cl_2 and excess $ClNO_3$) are then distilled off in vacuum at room temperature. The $Ti(NO_3)_4$ residue, in the form of a crystal cake, may be further purified by sublimation at 50°C.

PROPERTIES:

After sublimation slightly above the melting point, white needles. M.p. 58,5°C. Decomposes at about 100°C.

REFERENCES:

I. M. Schmeisser. Angew. Chem. 67, 493 (1955); D. Lützow, Thesis, Univ. of Munich, 1955.
II. W. Fink. Thesis, Univ. of Munich, 1956.

Thorium Nitrate

$Th(NO_3)_4 \cdot nH_2O$

RECOVERY OF THORIUM SALTS FROM MONAZITE

The mechanical ore-dressing process yields a monazite sand concentrate consisting of a mixture of Th silicate, rare earth phosphates, SiO_2 and usually 4–5% ThO_2. The material is calcined, finely ground and dissolved by prolonged digestion with conc. H_2SO_4 at 210°C. After cooling, the pasty mass is dissolved in ice water and the undissolved material is filtered off. Further treatment may proceed via the following methods.

I. In this method, Th is quantitatively precipitated as the phosphate, together with a small amount of rare earth phosphates; this is accomplished by neutralization and dilution of the solution. The phosphates are dissolved in conc. hydrochloric acid and precipitated with oxalic acid, and the thoroughly washed precipitate is extracted with warm aqueous Na_2CO_3. Most of the rare earths stay in the residue, while the thorium dissolves in the form of a carbonate complex, $Na_6Th(CO_3)_5$. The material is freed of the remaining traces of rare earths by repeated crystallization in the form of the sulfate $Th(SO_4)_2 \cdot 8H_2O$. The procedure consists of precipitation of the hydroxide with ammonia and solution of the latter in sulfuric acid to re-form the sulfate. The precipitate from the last purification stage is dissolved in nitric acid to yield the nitrate.

[In an older process, the Th and the rare earths are coprecipitated as oxalates from the initial acidic solution. The Th is extracted as the carbonatothorate by treatment with aqueous Na_2CO_3 solution.]

II. A good yield of ThO_2 may be obtained in another process used primarily for production of the rare earths. The filtered sulfate extract is treated with Na_2SO_4 to precipitate the cerium earths (as double sulfates); the corresponding Th salt $Na_2SO_4 \cdot Th(SO_4)_2 \cdot 6H_2O$ remains in solution. The mixture is filtered and the filtrate is heated to 90°C; it is treated with oxalic acid, yielding a precipitate consisting chiefly of Th oxalate.

Further treatment is the same as in method I.

III. PURIFICATION OF THORIUM NITRATE

Very pure NH_4NO_3 is added to a solution of the crude nitrate; the result is the double nitrate $Th(NO_3)_4 \cdot NH_4NO_3 \cdot 8H_2O$. The product is further purified by dissolving in triple-distilled water, adding redistilled nitric acid, and concentrating in a Pt dish on an electrically heated water bath until crystallization begins. The solution is then cooled with ice and constantly stirred; the resultant crystals are centrifuged off and redissolved. The procedure is repeated five times, yielding about 50% of the initial Th as the double nitrate.

The product is dissolved in very pure water, filtered and precipitated as the oxalate by addition of a nitric acid solution of purified oxalic acid; the precipitate is suction-filtered, washed with alcohol, and dried. The resultant Th oxalate may be calcined immediately to the oxide, or it may be reconverted to the nitrate by dissolving in conc. nitric acid.

IV. PREPARATION OF THE HYDRATES

Depending on the conditions of preparation, $Th(NO_3)_4$ crystallizes from solutions of thorium hydroxide (or from HNO_3 solutions of moderately calcined oxide) with varying contents of water of crystallization. When a not too acid solution is concentrated by evaporation, $Th(NO_3)_4$ crystallizes in the cold with 12 moles of H_2O. A solution evaporated at 15°C yields the pentahydrate, which is stable to 80°C if heated in an atmosphere free of CO_2. At higher temperatures, it converts to the trihydrate, and between 125 and 150°C, to the hemihydrate. Above 150°C the remaining water is split off, together with nitrogen oxides.

V. PREPARATION OF THE ANHYDRIDE

Anhydrous $Th(NO_3)_4$ is prepared by treatment of the lower hydrates of Th with N_2O_5 condensed at −78°C.

PROPERTIES:

Formula weights: $Th(NO_3)_4$ 480.15; $Th(NO_3)_4 \cdot 5H_2O$ 570.23. Very readily soluble in H_2O and alcohol. Due to hydrolysis, the aqueous solution becomes acid and slowly precipitates a basic salt. The commercial product usually contains about four moles of H_2O; it usually also contains some sulfate. Combines very readily with alkali and alkaline earth nitrates to yield double nitrates (very beautiful crystals). The alkali salts corresponding to the formula $Alk_2[Th(NO_3)_6]$ crystallize in anhydrous form, and the corresponding alkaline earth compounds with eight moles of H_2O. Water-containing alkali thorates $Alk[Th(NO_3)_5]$ have also been described.

REFERENCES:

I. D. W. Pearce, R. A. Hansen and J. C. Butler in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 38; see also H. and W. Biltz, Übungsbeispiele aus der unorganischen Experimentalchemie [Laboratory Problems in Experimental Inorganic Chemistry], Leipzig, 1920, p. 226; and L. Vanino, Handbuch der Präparativen Chemie [Handbook of Preparative Chemistry], Vol. I (Inorg. Part), Stuttgart, 1925, p. 759.

II. E. S. Pilkington and A. W. Wylie, J. Soc. Chem. Ind. 66, 387 (1947); this article also lists additional references on the subject.

III. O. Hönigschmid and S. Horovitz, Sitz.-Ber. Akad. Wissensch. Wien IIa, 125, No. 3 (1916); see also E. H. Archibald, The Preparation of Pure Inorganic Substances, New York, 1932, p. 193.

IV. E. Chauvenet and Souteyrand-Franck. Bull. Soc. Chim. France [4] 47, 1128 (1930).
V. P. Miscialeti. Gazz. Chim. Ital. 60, 882 (1930); see also J. R. Ferraro, L. J. Katzin and G. Gibson. J. Amer. Chem. Soc. 77, 327 (1955).

Titanium Oxonitrate, Zirconium Oxonitrate

$$TiO(NO_3)_2,\ ZrO(NO_3)_2$$

$$\underset{555.6}{TiI_4[ZrI_4]} + 4\,\underset{368.9}{N_2O_4} = \underset{295.9}{Ti(NO_3)_4}[\underset{339.3}{Zr(NO_3)_4}] + 4\,NO + 2\,I_2$$

$$\underset{295.9}{Ti(NO_3)_4}[\underset{339.3}{Zr(NO_3)_4}] = \underset{187.9}{TiO(NO_3)_2}[\underset{355.3}{ZrO(NO_3)_2}] + 2\,NO_2 + 1/2\,O_2$$

A suspension of TiI_4 or ZrI_4 in anhydrous CCl_4 is placed in a three-neck flask and agitated with a magnetic stirrer. Dry dinitrogen tetroxide is then bubbled through; the excess gas and the NO formed in the reaction are allowed to escape through a P_2O_5 tube. On contact with the gas, the liquid assumes a deep violet color due to liberation of iodine. After about one hour, the product is suction-filtered through a sintered glass plate; this operation is carried out in a dry box in flowing nitrogen (see Part 1, p. 71). The product is then washed with anhydrous CCl_4 and the solvent removed in vacuum.

PROPERTIES:

The almost white, powdery oxonitrates are hygroscopic; on heating, they are converted to the dioxides without melting. Soluble in alcohol, insoluble in benzene and CCl_4.

REFERENCE:

V. Gutmann and H. Tannenberger. Monatsh. Chem. 87, 424 (1956).

Titanium Phosphide, Zirconium Phosphides, Thorium Phosphide

$$TiP,\ ZrP_2,\ ZrP,\ Th_3P_4$$

Titanium Phosphide

I. The process recommended for the preparation of titanium phosphides is the pressure synthesis from the elements in the "Faradayi

apparatus (see Part I, p. 76).

$$\underset{47.9}{Ti} + \underset{31.0}{P} = \underset{78.9}{TiP}$$

Biltz et al. give the following procedure: 2 g. of Ti filings ground to pinhead size (for their preparation see the directions given for the lower titanium oxides, p. 1214) and 4 g. of red P are weighed into a small ceramic or sintered clay cylindrical crucible. The materials are degassed by fanning with a flame in high vacuum and are then sealed (in vacuum) into a quartz pressure tube. The colder half of the tube is heated to 450°C, while the Ti side is maintained at 950°C. Two three-day periods are needed for the reaction. After the first period, the tube is slowly cooled for 3-4 hours, and the unreacted P is thus distilled into the cooler section. The product is readily ground in an agate mortar, an indication that the ductile Ti metal has reacted. The grinding is carried out under CS_2, which is then removed with alcohol and by drying in vacuum over NaOH at 120-140°C. Microscopic examination of the dark-gray metallic product should show no red phosphorus. The phosphorus quantity used for the second reaction stage should again correspond to an atomic ratio of 3 P:1 Ti. The product treatment after the second three-day heating period is the same as that after the first. The resultant phosphide does not correspond completely to the formula TiP (maximum composition is $TiP_{0.92}$).

II.

$$\underset{189.7}{TiCl_4} + \underset{34.0}{PH_3} \rightarrow \underset{78.9}{TiP}$$

The method of Gewecke starts from phosphine generated from yellow P and KOH; the gas is washed with conc. hydrochloric acid to remove spontaneously igniting phosphorus hydrides, followed by NaOH. It is dried in two U tubes filled with $CaCl_2$ pieces (broken up from a solidified melt of the salt) and two P_2O_5 tubes. The gas enters the reaction apparatus proper through a trap (−250°C) designed in such a way that any gaseous $TiCl_4$ backing up during the reaction will condense out. The PH_3 train is connected to the reactor via a ground joint, with a two-way stopcock (for venting) inserted in the line.

The reactor consists of a a spherical $TiCl_4$ vessel followed by a heating tube 40 cm. long. Both the vessel and the tube are Vycor. The gases then flow into an ordinary glass receiving flask for $TiCl_4$ and absorption tubes for PH_3 (one contains aqueous $CuSO_4$ and the other copper wire mesh).

The system is first filled with H_2. The reaction tube is heated to 750°C and the PH_3 generator is started (this requires 3-4 hours). The $TiCl_4$, which is kept cold up to this time, is now heated.

The chloride vapor reacts with the phosphine in the hot reaction tube (reaction time: about three hours). As in the preparation of TiS_2 from $TiCl_4$ and H_2S, the $TiCl_4$ may be cycled back and forth through the tube. The titanium phosphide product is a light-gray, high-polish mirror deposited on the tube walls. However, the product is not free of the chloride even after treatment at 350°C in high vacuum. Preparations with maximum phosphorus content correspond to $TiP_{0.83}$; the yield is modest.

PROPERTIES:

Black-gray powder with a metallic appearance; attacked only slightly by acids even when heated; thermally very stable; it is assumed that a subphosphide exists, d 3.94.

REFERENCES:

W. Biltz, A. Rink and F. Wiechmann. Z. anorg. allg. Chem. 238, 395 (1938); I. Gewecke. Liebigs Ann. 361, 70 (1908); for data on the system $TiCl_4/PH_3$, see R. Höltje, Z. anorg. allg. Chem. 190, 246 (1930).

Zirconium Phosphides

The pressure synthesis used for TiP is also employed in the preparation of compounds of the Zr/P system. First stage: treatment in a Faraday tube for 50 hours at a 1000/500°C gradient; atomic ratio 1 Zr:4 P. Second stage: aftertreatment in a quartz pressure tube (wall thickness 4 mm., I.D. 12 mm.) for 50 hours at 800°C. The product is black-gray ZrP_2; this may be degraded to ZrP in high vacuum at 820°C. If the desired composition does not exceed $ZrP_{\leq 1}$, the second stage merely increases the homogeneity of the product. Since vapor pressure then ceases to be a factor, ordinary quartz tubes may be used.

The diphosphide ZrP_2 may also be prepared via method II for TiP.

REFERENCE:

E. F. Strotzer and W. Biltz. Z. anorg. allg. Chem. 239, 216 (1938).

Thorium Phosphide

One heating cycle in the Faraday apparatus suffices to prepare Th_3P_4 (a subphosphide $ThP_{0.8}$ also exists). The reactants are heated for 60 hours in a furnace with a 940/450°C gradient

atomic ratio of Th:P = 1:3). The absorptivity of Th for x-rays is very high, and therefore minute quantities of surface oxide interfere in the x-ray pattern analysis. Therefore, for precision work (particularly when the product is a lower phosphide) an empty cylindrical crucible is first heated for one hour (under high vacuum) in the rear section of the tubular quartz reactor, while the small quartz flask with the raw material at the front end of the reactor remains cold. After cooling of the rear section (in high vacuum), the raw material is transferred to the crucible and the reactor tube is sealed off.

REFERENCE:

E. F. Strotzer and W. Biltz. Z. anorg. allg. Chem. 238, 89 (1938).

Zirconium and Hafnium Phosphates

No unequivocal characterization exists for the phosphates precipitated from Zr salt solutions. The orthophosphate is formulated as either $Zr(HPO_4)_2$ or $ZrO(H_2PO_4)_2$; on prolonged heating above 700°C, it converts to ZrP_2O_7.

I. $$\underset{322.3}{ZrOCl_2 \cdot 8H_2O} \rightarrow \underset{301.2}{ZrO(H_2PO_4)_2} \rightarrow \underset{265.2}{ZrP_2O_7}$$

First, $ZrOCl_2 \cdot 8H_2O$ (2 g.) is dissolved in 1.5 liters of 6N HCl, and then a solution of 2 g. of Na_2HPO_4 in 1.5 liters of 6N HCl is added in drops. The finely divided precipitate is washed by repeated decantation with 6N HCl, filtered and dried at 80°C. The product corresponds to $ZrO(H_2PO_4)_2$.

The hafnium analogue, $HfO(H_2PO_4)_2$, is prepared in exactly the same manner; it is less soluble than the Zr salt.

II. *Alternate method:* Solutions of Zr sulfate (2–5% ZrO_2) and 2.5% H_3PO_4 in 2N sulfuric acid are added simultaneously in drops to 2N H_2SO_4 at 70–75°C.

PROPERTIES:

Sparingly soluble in conc. mineral acids, except hydrofluoric acid; when freshly precipitated, soluble (with formation of a complex) in a mixture of H_3PO_4, oxalic acid and conc. H_2SO_4. An acid-soluble, white peroxy compound is formed when a cold suspension of the phosphate is reacted with an $NaOH$–Na_2O_2 solution and then digested at 70°C. ZrP_2O_7 crystallizes in the cubic K 6_1 lattice.

REFERENCES:

I. G. Hevesy and K. Kimura. Angew. Chem. 38, 775 (1925); J. Amer. Chem. Soc. 47, 2540 (1925); see also J. H. de Boer, Z. anorg. allg. Chem. 144, 193 (1925).
II. E. M. Larsen, W. C. Fernelius and L. L. Quill. Analyt. Chem. 15, 512 (1943).

Titanium, Zirconium and Hafnium Carbides

TiC, ZrC, HfC

Titanium Carbide

Methods I to III, given in detail for the preparation of TiN, are also useful for synthesis of carbides. These are: I) the industrial process $TiO_2 + C$; II) synthesis from the elements; and III) vapor deposition. The last process may be modified by first depositing the metal from a vapor and then converting the deposit (on a glow wire) to the carbide by heating in a hydrocarbon atmosphere (method IV), or by using a glowing carbon wire in an atmosphere of $TiCl_4$ vapor (method V).

DropBooks

I. $$\underset{79.9}{TiO_2} + 3\,\underset{36.0}{C} = \underset{59.9}{TiC} + 2\,\underset{56.0}{CO}$$

In the method of Agte and Moers, a mixture of pure TiO_2 and acetylene-derived carbon black (the latter degassed at 2000°C) is placed in a graphite boat and heated for half an hour in a tubular graphite furnace to 1700–1800°C. Very pure and dry H_2 is used to flush the apparatus. Since the hydrogen reacts with the hot graphite tube to form hydrocarbons, the carbon content of the raw material mixture should be 15–25% less than the stoichiometric ratio. The products usually still contain some oxygen.

If the $TiO_2 + 3C$ mixture is heated very rapidly (within 20 minutes) to 1900°C in a stream of H_2 or CO, a product containing 19.5% C may be obtained (as demonstrated by Meyerson); further heating reduces the carbon content to 17%, because of decarbonization.

PRESINTERING

The carbide rods, made of powder compressed at 2000 kg./cm.², are heated in a graphite boat inside a tubular graphite furnace to temperatures between 2500 and 3000°C and maintained at these temperatures for about 15 minutes. The material is protected against surface absorption of additional carbon by embedding the rods in carbide powder.

Due to considerable shrinkage of the rods, the processes of repulverization, recompression and resintering must be repeated 3-4 times.

HIGH-TEMPERATURE SINTERING

Since the carbides decompose in vacuum, the high-temperature sintering must be carried out in an atmosphere of technical-grade argon. The rods are heated to extremely high temperatures—just short of the melting point (for a description of this procedure, see TiN, p. 1234). Most of the impurities evaporate at these temperatures, leaving a relatively pure product.

II. $$\underset{47.9}{Ti} + \underset{12.0}{C} = \underset{59.9}{TiC}$$

Titanium filings are mixed in the stoichiometric ratio with acetylene-derived carbon black (very thoroughly degassed at 2000°C), and the reaction is started by heating to 1800°C in a BeO boat placed inside a high-vacuum furnace (see Part I, p. 40 for description). The beryllium oxide boats are set up inside the heating element, which consists of tungsten boats (40 mm. long, 10 mm. wide, 8 mm. high) subjected to high-intensity (200 amp.) low-voltage current. The final sintering of the finely powdered crude product requires 10 minutes at 2400°C.

III. In this process a tungsten wire, which serves only as a substratum for the deposit, is heated to glowing in an atmosphere consisting of a volatile halide of the metal, a carbon compound and H_2. Moers recommends the use of hydrocarbons such as toluene, instead of CO; the deposition of free carbon with the carbide is avoided if the partial pressure of the hydrocarbon in the system is low. The hydrogen atmosphere facilitates considerably the reaction at the glow wire by reducing the decomposition temperatures of the halides to a much greater extent than does reduced pressure or even vacuum.

$$\underset{189.7}{TiCl_4} + \underset{16.0}{CH_4} \overset{(+\,H_2)}{=} \underset{59.9}{TiC} + \underset{145.8}{4\,HCl}$$

A pure hydrogen stream (which must be free of N_2 and O_2 and is therefore most conveniently generated by electrolysis) is divided into two fractions, one of which is passed through a 25°C wash bottle filled with $TiCl_4$, the other through a similar bottle containing toluene at −15°C; the streams are then recombined and introduced into the reactor. The glow wire is maintained at a temperature of 1500°C, which is kept constant during the experiment by gradually increasing the current. Further details are given by K. Moers.

Alternate methods:

IV. A modification of the method just described consists in heating the metal wire prepared by the vapor deposition process in a hydrocarbon atmosphere. This modification is not, however, very convenient in the case of the lower-melting metals (Ti, Zr) since the wire temperatures must be relatively low and thus very long glow times are required. It may be used successfully with W, Ta and Hf.

V. Another method of avoiding introduction of the tungsten wire (which is used as a substratum in all previously described vapor deposition processes) into the product reverses the above procedure; i.e., a carbon wire is heated to incandescence in the vapor of a volatile halide of the metal (in the presence or in the absence of H_2).

The method suffers from one disadvantage: the dissociation of the chlorides at the glow wire does not cease when all the carbon originally present in the wire has been consumed. As a result, the products contain varying amounts of the free metal dissolved in the carbide. Carbides of stoichiometric composition are obtained either by calcining the above products in high vacuum (to evaporate the dissolved metal) or in a hydrocarbon atmosphere (to convert the excess metal to carbide). Further details are given in the reference cited below.

DropBooks

PROPERTIES:

Gray powder. Insoluble in hydrochloric acid, soluble in nitric acid. M.p. 3410°C; d 4.92. Very good electrical conductor with a positive temperature coefficient. Crystal structure: type B1 (NaCl type), with a considerable range of phase compositions ($TiC_{1.0}$-$Ti_{0.3}$).

Zirconium Carbide and Hafnium Carbide

These compounds are prepared by the same procedures as titanium carbide. The reaction mixture consists of either ZrO_2 (or HfO_2) + 3 C, or Zr (or Hf) + C; the reaction temperatures lie above 2000°C. Since both ZrC and HfC are very sensitive to N_2, the high-temperature sintering stage must be carried out in 99% Ar.

Just like TiC, both ZrC and HfC dissolve carbon when molten. This phenomenon is most detrimental in the case of ZrC, whose melting point is lowered from 3500°C to about 2450°C by the absorption of carbon; the carbon is released on cooling.

The procedures employed for the preparation of TiC by the vapor deposition process must be modified somewhat in the case of ZrC and HfC, since both $ZrCl_4$ and $HfCl_4$ are solids. The

reactor is filled with a sufficient quantity of the chloride and its lower section is heated with a small furnace to a temperature at which the vapor pressure is about 10–20 mm. (that is, to about 300°C). The same applies in method V.

The industrial preparation of ZrC from $ZrSiO_4$ and carbon in a graphite crucible using an arc furnace is described by W. Kroll et al. [Trans. Electrochem. Soc. 89, 263, 317 (1946); 92, 187 (1947); J. Electrochem. Soc. 94, 1 (1948)].

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I. G. A. Meyerson and Y. M. Lipkes. Zh. Prikl. Khimii 18, 24, 251 (1945); see also E. Friederich and L. Sittig. Z. anorg. allg. Chem. 144, 169 (1925).
II. P. Ehrlich. Z. anorg. Chem. 259, 1 (1949).
III and IV. A. E. van Arkel and J. H. de Boer. Z. anorg. allg. Chem. 148, 345 (1925).
V. W. G. Burgers and J. C. Basart. Z. anorg. allg. Chem. 216, 209 (1934).

Thorium Carbides

ThC, ThC_2

$$\underset{264.1}{ThO_2} + \underset{36.0}{3C} = \underset{244.1}{ThC} + \underset{56.0}{2CO}; \quad \underset{264.1}{ThO_2} + \underset{48.0}{4C} = \underset{256.1}{ThC_2} + \underset{56.0}{2CO}$$

Thorium carbides are prepared in an electric arc furnace. The arc is produced in a graphite crucible containing the reaction mixture. About 200 amp. at 110 v. is required to melt the mixture.

A mixture of ThO_2 and calcined carbon black (0.24% ash) or graphite powder (0.33% ash), in quantities corresponding to the above equations, is made into a paste with a small amount of water and starch, and evaporated with stirring (graphite is preferred to carbon black because of its smaller volume). The lumps of dried material are placed in a crucible by means of a porcelain spatula; their large size prevents them from being carried out of the crucible by the CO gas evolved in the process.

PROPERTIES:

ThC: Opaque, dark-yellow pseudotetragonal crystals with a metallic luster. M.p. 2650°C; d 8.96. Completely miscible with

ThC at high temperature, practically immiscible at room temperature. Forms a eutectic with graphite (empirical formula $ThC_{2.9}$, m.p. 2500°C). Decomposes slowly in water, rapidly in dilute acids, evolving a mixture of hydrocarbons (chiefly acetylene) and H_2.

ThC: M.p. 2620°C. Crystal structure: NaCl type. For material of empirical formula $ThC_{0.39}$, the miscibility gap begins at a temperature of 1980°C; the gap widens at room temperature to $ThC_{0.05}$-$ThC_{0.78}$.

REFERENCES:

M. von Stackelberg, Z. phys. Chem. (B) 9, 437 (1930); H. A. Wilhelm and P. Chiotti, Trans. Amer. Soc. Metals 42, 1295 (1950).

Titanium, Zirconium and Thorium Silicides

$TiSi_2$, $ZrSi_2$, $ThSi_2$

I. PREPARATION FROM THE ELEMENTS

Ti (Zr, Th)	+	2 Si	=	$TiSi_2$ ($ZrSi_2$, $ThSi_2$)			
47.9	91.2	232.1		56.1	104.0	147.3	288.2

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The silicides are prepared by fusing or sintering intimate stoichiometric mixtures of the elements (in powder form). The reaction is carried out in sintered clay or ceramic crucibles, placed in a Tammann furnace under a blanket of Ar. In all three cases the reaction takes place at a relatively low temperature and is highly exothermic; therefore, one should work with gram quantities only.

In the method of Alexander, some advantage is gained by replacing the pure metals with hydride powders. Initial heating takes place in vacuum, which at 400-500°C is replaced by an atmosphere of the H_2 evolved by the reaction itself. This gives a sintered silicide at temperatures as low as 900°C.

Brauer and Mitius modified a method developed by Hönigschmid and prepare $ThSi_2$ by the following procedure. Intimate mixtures of Al, Th and Silumin (13% Si, 87% Al) powders are compressed into tablets 10 mm. long and 5 mm. thick, placed in alumina crucibles and fused at 1100°C in high vacuum. Slow cooling (from 1100°C to 800°C in four hours) produces good crystals of the product within the aluminum ingot. These are freed of excess Al by alternate treatments with dilute hydrochloric acid and potassium hydroxide (moderate heating), followed by washing with water and alcohol. Since most of the silicide particles form cohesive

granules with the Si and SiO_2 contaminants, the crystallites are pulverized in an agate mortar and separated from foreign matter (particularly SiO_2, which cannot be removed by chemical means) by flotation with bromoform (d 2.9). The bromoform must be continuously renewed. Evaporation with hydrofluoric acid is not practical, since it destroys the silicide.

Alternate methods:

II. ALUMINOTHERMIC METHOD

Ignition of a mixture of, for example, 200 g. of Al powder, 250 g. of S, 180 g. of SiO_2 and 15 g. of TiO_2 (or 40 g. of K_2TiF_6), covered with a thin layer of Mg, yields an ingot containing, in addition to Si and Al, small, iron-gray tetragonal pyramids of $TiSi_2$.

III. ELECTROLYTIC PREPARATION

The pure, crystalline silicides are obtained by melt electrolysis of a mixture of, for example, 10 K_2SiF_6 + TiO_2 at about 900°C, using an iron cathode; alternately, electrolysis of TiO_2 dissolved in a melt of silicate may be used.

IV. REACTION OF THE METAL WITH SILICON TETRACHLORIDE

The silicides are obtained in the form of a coating on the reactor walls when the metals are heated to 1100–1500°C in a hydrogen stream saturated with $SiCl_4$.

PROPERTIES:

Grayish-white crystals with a metallic luster and good thermal and electrical conductivity. d ($TiSi_2$) 4.02; ($ZrSi_2$) 4.88; ($ThSi_2$) 7.63. $TiSi_2$ and $ZrSi_2$ are insoluble in mineral acids (except hydrofluoric acid); $ZrSi_2$ is also insoluble in 10% KOH. $TiSi_2$ dissolves slowly in 10% KOH. $ThSi_2$ is unaffected by alkali, but dissolves in dilute and conc. hydrogen halides (slowly in the cold and rapidly when heated). Attacked by Cl_2 at temperatures as low as 500°C. $TiSi_2$ is stable at red heat in air, while $ZrSi_2$ and $ThSi_2$ burn.

REFERENCES:

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II. O. Hönigschmid. Comptes Rendus Hebd. Séances Acad. Sci. 142, 157, 280 (1906); Monatsh. Chem. 27, 205, 1069 (1906).
III. M. Dodero. Comptes Rendus Hebd. Séances Acad. Sci. 208, 799 (1939); J. L. Andrieux. Congr. Chim. Industr. Nancy 18 I, 124 (1938); Rev. Métallurgie 45, 49 (1948).

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SECTION 23

Vanadium, Niobium, Tantalum

G. BRAUER

Vanadium

V

The preparation of high-purity V metal is difficult because it tends to form very stable occluded phases with nonmetals, particularly with O, N and C. These elements must be removed in advance, because their elimination from the metal phase at a later stage is difficult. Hence only a few of the many proposed methods afford a ductile metal or V powder of a high degree of purity.

I. $$\underset{181.9}{V_2O_5} + \underset{200.4}{5\,Ca} = \underset{101.9}{2\,V} + \underset{280.4}{5\,CaO}$$

In the method of Marden and Rich, 175 g. of V_2O_5 is mixed with 300 g. of ground Ca and 300 g. of $CaCl_2$ (dehydrated by preheating at 450°C), and the mixture placed in a small sealable iron bomb. The addition of $CaCl_2$ as fluxing agent is essential. A small piece of Na or K is also added (to act later as a scavenger for residual O_2 and H_2O), or the bomb is evacuated and then filled with Ar. The bomb is tightly sealed either by screwing down the lid or by welding, heated one hour at 900–950°C, cooled *to room temperature* and then reopened. The product is chipped out with a chisel, and the chunks are added, slowly and with agitation, to about 20 liters of cold water (avoid local overheating). The product disintegrates and is allowed to settle for about 2 min. The supernatant is decanted; the solid is washed (by decantation) several times with H_2O, then several times with approximately 2 N HCl. The product is ductile, granular V metal.

According to McKechnie and Seybolt, the reaction between V_2O_5 and Ca is coupled to advantage with the strongly exothermic reaction $Ca + I_2 = CaI_2$. In this case, CaI_2 has the desirable effect of reducing the melting point of the mixture, thus replacing the $CaCl_2$ used in the previous method.

For example, a mixture of 300 g. of specially purified V_2O_5 (see below), 552 g. of metallic Ca (i.e., about 60% excess) and 150 g. of

I_2 is placed in a sintered magnesia crucible, which is in turn placed in a 1.5-liter steel bomb; the bomb is then hermetically sealed. With the above quantities, the steel bomb should have a diameter of 100 mm., a height of 280 mm. and a 10-mm.-thick wall; the lid should be a steel plate held between bolted-down flanges. The magnesia crucible can be closed with a cover of the same material (the cover is formed by pressure-shaping granular magnesia with a steel cover). The bomb is evacuated, filled with Ar, closed and heated to about 425°C to start the reaction. Immediately after ignition, spontaneous heating to a much higher temperature takes place, accompanied by an unusual noise. Granular and powdered V is isolated from the reaction product in 74% yield.

The V_2O_5, which is normally prepared from NH_4VO_3, must be freed before use of small amounts of N and H still adhering to it. One method of accomplishing this is heating the oxide for 18 hours in a stream of moist O_2 at 400°C.

II. The following reduction affords V as a fine powder:

$$\underset{157.3}{VCl_3} + \underset{33.6\ l.}{1\tfrac{1}{2}H_2} = \underset{51.0}{V} + \underset{109.4}{3HCl}$$

A stream of H_2, thoroughly freed of traces of O_2, N_2 or H_2O (see p. 112 ff., N_2 removal as for Ar, p. 82 ff.), is passed over a platinum boat located in a Pt tube and containing about 7 g. of VCl_3. The Pt tube forms an insert for a porcelain tube and protects the latter from attack by the subliming VCl_3 and by the V formed from such a sublimate; it also ensures the protection of the boat contents from contamination by Si compounds from the porcelain tube. The V formed during the reaction is further protected against contamination by placing a porcelain boat containing powdered V ahead of the Pt boat. This protective vanadium (which may be less pure) serves to remove the last traces of N_2 and O_2 from the gas stream. The reactor tube is connected to a large, empty U tube which allows observation of the exit gas and is, in turn, connected to a KOH-filled trap.

The porcelain tube is slowly heated to, and then held at, a temperature of 900°C until HCl evolution (which follows the initial formation of a small quantity of brown fumes) is complete. After cooling to room temperature (and not before), the product is removed from the reactor in a stream of H_2. At this point, it consists of vanadium hydride (approximate composition $VH_{1.7}$), which is converted to pure V by heating in high vacuum. It should be borne in mind that finely subdivided vanadium and vanadium hydride are sensitive to atmospheric O_2 even at room temperature.

The Pt sheet absorbs some V during the reaction and turns darker, brittle and fragile. The vanadium can be removed from

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the Pt in the form of V_2O_5 by heating to red heat in air or, via a more drastic method, by treatment with a molten mixture of 1 part of KNO_3 and 15 parts of $NaKCO_3$. The Pt is thus completely regenerated. It should be possible to replace the porcelain tube, with no loss of efficiency, by an alumina tube.

Alternate methods: a) Very pure V can be obtained by deposition from the gas phase in the apparatus shown in Fig. 291, p. 1168. In this case the apparatus is made of fused quartz and is heated to 900-1000°C during the reaction. A suitable crude metal starting product is obtained, for example, by reacting a mixture of VCl_3 and Na in a heated iron bomb. Since the transport to the incandescent wire is accomplished via VI_2, whose volatility is relatively low, this process is not as advantageous in the case of V as with metals of Group IV [A. E. van Arkel, Metallwirtsch. 13, 405 (1934); J. W. Nash, H. R. Ogden, R. E. Durtschi and I. E. Campbell, J. Electrochem. Soc. 100, 272 (1953); H. W. Rathmann and H. R. Grady, Vancoram Rev. 10, 6, 17 (1955)].

b) With Ar as the carrier phase, the reduction of VCl_4 with H_2 (affording pure V powder) can be accomplished at 620°C [G. Jantsch and F. Zenek, Monatsh. Chem. 84, 1119 (1953)].

c) According to another proposed method, a stream of dry, high-purity H_2 saturated with VCl_4 vapor is passed over Mg turnings (in a MgO boat) and gradually heated to 700°C over a period of 2.5 hours. After cooling, the product mixture of V, VCl_2 and VCl_3 is thoroughly extracted with H_2O to dissolve out any chlorides present. The residue of V powder (99.3% V) is then vacuum-dried.

d) A mixture of 2 parts of VCl_2 and 1 part of Mg is pressed into pellets and these are heated for 1-2.5 hours at 700°C in a MgO boat inserted in a quartz tube (H_2 or Ar atmosphere). The product metal contains up to 99.5% V [A. Morette, Comptes Rendus Hebd. Séances Acad. Sci. 200, 1110 (1935)].

Solid V metal is comminuted and reduced to a fine powder via the vanadium hydride stage. Thus, vanadium is heated to about 500°C in a stream of high-purity H_2 and is then cooled in the same gas. The hydride is very brittle and can be readily comminuted by pounding or grinding in a volatile organic liquid such as benzene, which protects it against local heating and oxidation. The comminuted material is then dehydrogenated to pure V metal by heating in high vacuum (W. D. Schnell, Thesis, Univ. of Freiburg i. Br., 1960).

The purity of high-grade V can be further increased (to about 99.997%) by long heating (e.g., for 20 hours) in a high vacuum (10^{-5} mm.) at 1650°C (W. D. Schnell, Thesis, Univ. of Freiburg i. Br., 1960).

For information concerning melting V metal in crucibles made of various materials, see T. W. Merril, Vancoram Rev. 11, 11, 16 (1956).

PROPERTIES:

Atomic weight 50.95. Light-gray metal, ductile when pure. M.p. 1900°C; d 6.11. Insoluble in hydrochloric and sulfuric acids, soluble in nitric and hydrofluoric acids. High affinity for O, N, C and H. Surface reaction with atmospheric O_2 starts already at 20°C; this can lead, particularly in the case of a fine powder, to considerable contamination. Crystal structure: type A_2.

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I. J. W. Marden and H. C. Rentschler. Ind. Eng. Chem. 19, 97 (1927); E. D. Gregory, W. C. Lilliendahl and D. M. Wroughton. J. Electrochem. Soc. 98, 395 (1951); A. P. Beard and D. D. Crooks. J. Electrochem. Soc. 101, 597 (1954); R. K. McKechnie and A. U. Seybolt. J. Electrochem. Soc. 97, 311 (1950); J. R. Long. Iowa State Coll. J. Sci. 27, 213 (1953).

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Vanadium (II) Chloride

VCl_2

I.

$$\underset{157.3}{VCl_3} + \underset{11.2\ l}{{}^1/_2 H_2} = \underset{121.9}{VCl_2} + \underset{36.5}{HCl}$$

The reactor is a Pyrex, Vycor or fused quartz tube, and the VCl_3 is placed either directly in the tube or in a porcelain boat (the transfer to the reactor requires great care, because VCl_3 is very hygroscopic). A stream of dry, completely deoxygenated hydrogen is then passed through the tube (the end of the tube is protected against moisture by a $CaCl_2$ tube), and the system is heated to about 400°C. While HCl is evolved, the temperature is gradually increased to 675°C. Care should be taken not to exceed 700°C (according to Klemm and Hoschek, not even 500°C), otherwise reduction to V metal will occur. The reaction time depends on the quantity of material used; it is about 1 hour for 0.5 g., and about 40 hours for 30 g. At the end of the reaction, the H_2 stream is replaced by a stream of P_2O_5-dried N_2 or CO_2, and the VCl_2 produced is discharged from the reactor under anhydrous conditions. A high yield (~90%) is obtained.

II.

$$\underset{314.6}{2\,VCl_3} = \underset{121.9}{VCl_2} + \underset{192.8}{VCl_4}$$

Rapid disproportionation of VCl_3 according to the above equation can be achieved at 800°C in a stream of high-purity N_2. The VCl_4

is carried away by the N_2 stream (4 bubbles/sec.), while the VCl_3 remains in the reactor tube. The temperature should not exceed 850°C, to avoid loss of VCl_3 by sublimation. The reaction is fairly fast; for example, the reaction of 20 g. of VCl_3 takes 2 hours.

PROPERTIES:

Light-green leaflets; m.p. about 1350°C; d. 3.09. Less hygroscopic than VCl_3 and VCl_4; insoluble in alcohol or ether. Crystal structure: CdI_2 type.

REFERENCES:

I. F. Ephraim and E. Ammann, Helv. Chim. Acta 16, 1273 (1933); W. Klemm and E. Hoschek, Z. anorg. allg. Chem. 226, 359 (1936); R. C. Young and M. E. Smith in: J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 126; H. Funk and W. Weiss, Z. anorg. allg. Chem. 295, 327 (1958).
II. O. Rugg and H. Lickfett, Ber. dtsch. chem. Ges. 44, 506 (1911); P. Ehrlich and H. J. Seifert, Z. anorg. allg. Chem. 301, 282 (1959).

Vanadium (III) Chloride

VCl_3, $VCl_3 \cdot 6\,H_2O$

VCl_3

I. $$\underset{149.9}{V_2O_3} + 3\,\underset{356.9}{SOCl_2} = 2\,\underset{314.6}{VCl_3} + 3\,\underset{192.2}{SO_2}$$

Vanadium trioxide powder (2.1 g.) and 8.5 ml. of pure $SOCl_2$ are placed in a bomb tube about 1.5 cm. in diameter, and the sealed tube is heated for 24 hours at 200°C. The tube is cooled to below 0°C (in order to lower the SO_2 vapor pressure) and is then opened to allow SO_2 to escape. Then the tube contents are flushed out, under anhydrous conditions, into a small flask, using some $SOCl_2$ for this purpose (the $SOCl_2$ is then removed by vacuum distillation). The VCl_3 residue is washed several times with very pure CS_2 to remove traces of S_2Cl_2, and then thoroughly vacuum-dried at 80°C. Fine crystals of dark-violet VCl_3 are obtained in nearly quantitative yield.

II. $$\underset{363.8}{2\,V_2O_5} + 6\,\underset{810.2}{S_2Cl_2} = 4\,\underset{629.3}{VCl_3} + 5\,\underset{320.3}{SO_2} + 7\,\underset{224.4}{S}$$

Fine, pure V_2O_5 powder (18 g.) and 40 ml. of S_2Cl_2 are refluxed under anhydrous conditions for 8 hours (constant stirring). The

excess S_2Cl_2, containing dissolved S, is decanted and the VCl_3 formed is washed with dry CS_2. Adhering volatiles are removed by heating the material at 120–150°C under vacuum or by extracting it for several hours with CS_2 in a Soxhlet apparatus. After thorough purification, the residual sulfur content of the resulting fine crystals of VCl_3 is about 0.2%. The yield is about 30 g.

Coarse (and hence less hygroscopic) crystals of VCl_3 are obtained by heating the fine crystalline product with a small amount of fresh S_2Cl_2 in a sealed tube at 240°C. Since no gas is evolved in this operation, large amounts can be treated at one time.

The same reaction can also be carried out in a sealed tube at 300°C; however, smaller quantities must be used in this case (6–7 g. of V_2O_5 and 20 ml. of S_2Cl_2).

III.
$$\underset{192.8}{VCl_4} = \underset{157.3}{VCl_3} + \underset{35.5}{{}^1/_2Cl_2}$$

A flask containing VCl_4 is connected to a reflux condenser via a ground joint and kept at 160–170°C for 2 days while passing a thoroughly dried and deoxygenated stream of CO_2 or H_2 through the system (to remove the Cl_2 formed in the thermal dissociation). The flask is then arranged for distillation; unreacted VCl_4 and the traces of the $VOCl_3$ formed are distilled off at 200°C in a H_2 stream. Reduction does not take place under these conditions. The by-products can also be removed by vacuum distillation. All operations are carried out under anhydrous conditions.

Alternate methods: IV. Reaction of VCl_4 with S, removal of the S_2Cl_2 by distillation, then heating of the product at a temperature somewhat below 300°C in a stream of CO_2.

V. If V metal is available as a very fine powder, it can be reacted with excess ICl, according to the equation:

$$\underset{101.9}{2V} + \underset{974.2}{6ICl} = \underset{761.5}{3I_2} + \underset{314.6}{2VCl_3}$$

The mixture is heated under anhydrous conditions in a glass flask equipped with a reflux condenser. The flask is carefully heated with a direct flame until the initially vigorous reaction, which affords iodine vapor, subsides and vapors of the boiling ICl become visible. After cooling, the mixture is extracted with CCl_4 (distilled from P_2O_5), filtered in a N_2 stream through a sintered glass disk, washed with CCl_4 and dried in a vacuum desiccator. The product is very pure provided all of the vanadium has reacted.

PROPERTIES:

Formula weight 157.3. Violet, quite crystalline. Very hygroscopic. Soluble in acidified water. In the absence of air, can be

obtained from solutions as $VCl_3 \cdot 6H_2O$. Soluble in alcohol, insoluble in ethyl ether. d 3.0. Crystal structure: $D0_5$ ($FeCl_3$) type.

REFERENCES:

I. H. Hecht, G. Jander and H. Schlapmann. Z. anorg. Chem. 254, 255 (1947); experiments carried out at the University Laboratory, Freiburg i. Br., 1951.
II. H. Funk and C. Müller. Z. anorg. allg. Chem. 244, 94 (1940); experiments carried out at the University Laboratory, Freiburg i. Br., 1951; H. Hartmann and H. L. Schläfer. Z. Naturforsch. 6a, 754 (1951); H. Funk and W. Weiss. Z. anorg. allg. Chem. 295, 327 (1958).
III. J. Meyer and R. Backa. Z. anorg. allg. Chem. 135, 177 (1924); F. Ephraim and E. Ammann. Helv. Chim. Acta 16, 1273 (1933); R. C. Young and M. E. Smith in: J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-Toronto-London, 1953, p. 128.
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V. V. Gutmann. Monatsh. Chem. 81, 1155 (1950).

$VCl_3 \cdot 6H_2O$

The hexahydrate can be obtained from aqueous, acidic VCl_3 solution by cooling and saturating with HCl. The starting solution is obtained by electrolytic reduction of a solution of V_2O_5 in hydrochloric acid or, more conveniently, by dissolving V_2O_3 in hydrochloric acid.

$$\underset{181.9}{V_2O_5} + 2\,\underset{44.8\ l.}{H_2} = \underset{149.9}{V_2O_3} + 2\,H_2O$$

$$\underset{149.9}{V_2O_3} + 6\,\underset{134.4\ l.}{HCl} + 9\,\underset{162.1}{H_2O} = 2\,\underset{265.4}{VCl_3 \cdot 6\,H_2O}$$

For example, 7.5 g. of V_2O_3 (obtained by reduction of V_2O_5 with H_2 as described on p. 1267) is dissolved in 200 ml. of conc. HCl by allowing the mixture to boil several hours. This solution is concentrated to 50 ml., cooled to −10 to −20°C, and saturated with HCl gas. The precipitate of green $VCl_3 \cdot 6\,H_2O$ is suction-filtered on glass frit, dissolved in some H_2O, and reprecipitated with HCl while cooling (see also the preparation of $TiCl_3 \cdot 6\,H_2O$, p. 1193 f.).

PROPERTIES:

Formula weight 265.4. Green, hygroscopic crystals.

REFERENCES:

A. Piccini and M. Brizzi. Z. anorg. Chem. 19, 394 (1899); P. Ehrlich and H. J. Seifert, Z. anorg. allg. Chem. 301, 282 (1959).

Vanadium (IV) Chloride

VCl_4

I.

$$\underset{157.3}{VCl_3} + \underset{11.2\ l.}{{}^1/_2 Cl_2} = \underset{192.8}{VCl_4}$$

In the method of Funk and Weiss VCl_3, which is readily obtained from V_2O_5 and S_2Cl_2 (see p. 1256), is loosely packed in a slightly inclined reactor tube made of high-melting glass. The tube is connected by a ground joint to a receiver, which is protected against moisture. A glass-wool wad is placed at the end of the reactor tube to prevent solid VCl_3 particles from reaching the receiver. Dry Cl_2 is passed through the apparatus to displace the air; the VCl_3 is then heated, starting from the end closest to the receiver. The reaction rate can be controlled by regulating the Cl_2 flow. The crude VCl_4 is collected in the receiver, which is kept at 0°C; it is then distilled from this receiver in a slow stream of Cl_2 (anhydrous conditions), discarding the forerun. Approximately 35 g. of pure VCl_4 is obtained from 30 g. of VCl_3.

II. A process similar to that described in method I may be used to prepare VCl_4 from ferrovanadium and Cl_2. A very long reactor tube is used, and the reaction rate is regulated so as to allow most of the by-product $FeCl_3$ to settle out. The VCl_4 must be redistilled from the receiver.

Alternate method: Disproportionation of VCl_3 to VCl_2 and VCl_4 by heating in a N_2 stream at 900°C in a porcelain tube [O. Ruff and H. Lickfett, Ber. dtsch. chem. Ges. 44, 506 (1911)].

PROPERTIES:

Dark red-brown liquid. M.p. −109°C, b.p. 148.5°C; d 1.87. Fumes in air, and even at normal temperature shows a marked Cl_2 vapor pressure (decomposition). Sealed ampoules containing VCl_4 should be stored in the dark (occasionally they shatter because of high internal pressure). Decomposed by water. Soluble in conc. hydrochloric acid, ethanol and ethyl ether.

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I. H. Funk and W. Weiss. Z. anorg. allg. Chem. 295, 327 (1958).
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Vanadium (II) Bromide

VBr_2

$$\underset{290.7}{VBr_3} + \underset{11.2\ l.}{{}^1/_2 H_2} = \underset{210.8}{VBr_2} + \underset{80.9}{HBr}$$

The starting material is VBr_3, which is best left in the tube used for its preparation (see below). In this case, the reactor tube is considerably longer than that used merely to prepare VBr_3.

The zones containing VBr_3 are heated, one after another, to dark-red heat while a H_2 stream is passed through. The heating is best accomplished in a tubular electric furnace, in which heating is more uniform than with open flames; with such a furnace, pronounced local overheating and reaction rate differentials are prevented and the total reduction time is short. The reduction of 2 g. of VBr_3 takes 1–1.5 hours.

PROPERTIES:

Light-brown to reddish; light pink-red when heated. Feltlike to flaky crystal aggregates. More hygroscopic than VCl_2, but not as sensitive as VBr_3. Gives a violet solution with H_2O; this soon turns brown, evolving H_2. d 4.58. Crystal structure: C6 (CdI_2) type.

REFERENCES:

F. Ephraim and E. Ammann, Helv. Chim. Acta 16, 1273 (1933); W. Klemm and E. Hoschek, Z. anorg. allg. Chem. 226, 359 (1936).

Vanadium (III) Bromide

VBr_3

$$\underset{51.0}{V}\ (+\ \underset{55.9}{Fe}) + \underset{239.7}{{}^3/_2 Br_2}\ (+\ \underset{239.7}{{}^3/_2 Br_2}) = \underset{290.7}{VBr_3}\ (+\ \underset{295.6}{FeBr_3})$$

A high-melting glass tube, 10–12 mm. I.D. and 80 cm. long, is charged with 5 g. of very finely powdered high-grade ferrovanadium (no boat is used). A stream of thoroughly dried CO_2 is passed through a small round-bottom flask in which absolutely dry Br_2, slowly introduced from a dropping funnel, is vaporized by slight heating. The CO_2 and Br_2 vapors then pass through the reactor tube. The other end of the reactor carries (preferably sealed on) containers for the subsequent collection of VBr_3 (e.g., tubes which can be melt-sealed), which are protected from the atmosphere by a P_2O_5

tube. Air and moisture must be rigorously excluded. After filling the reactor with $CO_2 + Br_2$, the Fe-V is heated to red heat. The first product is a small amount of $VOBr_3$, which is quickly and readily displaced by heating the entire tube length to prevent the deposition of vanadium oxide (the latter cannot be removed). The conversion to VBr_3 and $FeBr_3$ is then carried out over a period of about 4 hours. Most of the $FeBr_3$ remains at the exit end of the tube, while the Br_3 sublimes out. It is freed of $FeBr_3$ by repeated sublimation. Rather low sublimation temperatures and long sublimation tubes are required in this procedure. Finally the system is flushed with pure, Br_2-free CO_2.

PROPERTIES:

Black with greenish reflections, crystalline; the vapor is violet. Extremely hygroscopic. d 4.52.

REFERENCES:

J. Meyer and R. Backa, Z. anorg. allg. Chem. 135, 177 (1924); F. Ephraim and E. Amman, Helv. Chim. Acta 16, 1273 (1933); W. Klemm and E. Hoschek, Z. anorg. allg. Chem. 226, 359 (1936).

DropBooks

Vanadium (II) iodide

VI_2

This compound is prepared by synthesis from the elements.

$$\underset{51.0}{V} + \underset{253.8}{I_2} = \underset{304.8}{VI_2}$$

I. In the method of Morette, VI_3 is first prepared from V and I_2 (see the following preparation) and then decomposed by heating at 400°C in high vacuum while removing the I_2 split off. The decomposition is virtually complete in 24 hours.

II. In the method of Klemm and Grimm, a stoichiometric mixture of V turnings and I_2 is sealed under vacuum into a short quartz tube, with occasional cooling to reduce the I_2 vapor pressure. The entire tube is then uniformly heated at 160-170°C.

PROPERTIES:

Dark-violet, hexagonal leaflets. Not readily wetted by H_2O; slowly forms a violet solution. Insoluble in absolute ethanol, benzene, CCl_4, CS_2. Partly oxidized in air, turning brown. d 5.44. Crystal structure: C6 (CdI_2) type.

REFERENCES:

A. Morette, Comptes Rendus Hebd. Séances Acad. Sci. 207, 1218 (1938); W. Klemm and L. Grimm, Z. anorg. allg. Chem. 249, 198 (1942).

Vanadium (III) Iodide

VI_3

Formed when metallic V and I_2 are heated at 300°C under the vapor pressure generated by the latter.

$$\underset{51.0}{V} + \underset{380.7}{^3/_2 I_2} = \underset{431.7}{VI_3}$$

Vanadium metal (turnings or powder) and excess I_2 are placed in a hard glass or fused quartz tube, closed at one end; the tube contents are cooled to −80°C; the tube is thoroughly evacuated and then melt-sealed to a short total length. A vigorous reaction sets in on heating. The entire tube is heated for a while at temperatures up to 300°C in order to achieve product uniformity. The excess I_2 is then allowed to distill off into a somewhat cooler zone, and the tube is quickly cooled and opened.

PROPERTIES:

Brown-black, crystalline powder. Very hygroscopic. Readily soluble in water giving a brown solution which turns gradually green in air. Also soluble in absolute ethanol; insoluble in benzene, CCl_4, CS_2. d 4.2.

REFERENCE:

A. Morette, Comptes Rendus Hebd. Séances Acad. Sci. 207, 1218 (1938).

Vanadium Oxychloride

VOCl

$$\underset{149.9}{V_2O_3} + \underset{157.3}{VCl_3} = \underset{307.2}{3\,VOCl}$$

A quartz tube, about 180 mm. long and 15 mm. in diameter, is charged with 1 g. of V_2O_3 and 2 g. of VCl_3 under anhydrous

conditions. The tube is thoroughly evacuated, melt-sealed and placed horizontally in a furnace providing a temperature gradient such that the raw material is kept at 720°C and the empty half of the tube at 620°C (see Part I, p. 76 f. and preparation of $TiOCl_2$, p. 1209). After 1–2 days, VOCl forms as a crystalline deposit in the center of the tube and a dense mass on the 720°C side. In addition, small amounts of VCl_2, VCl_3, VCl_4 and $VOCl_3$ are also present. The tube is opened in dry N_2, and the VCl_4 and $VOCl_3$ are vaporized in vacuum. The tube contents are then slurried in dimethylformamide, and the VCl_2 and VCl_3 are removed from the VOCl by repeated slurrying and decantation with this solvent. The VOCl, obtained as the residue, is washed with ethanol and ethyl ether and vacuum-dried.

Alternate methods: Vanadium oxychloride can also be obtained a) by heating VCl_3 and CO_2 [O. Ruff and H. Lickfett, Ber. dtsch. chem. Ges. 44, 506 (1911); E. Wedekind and C. Horst, Ber. dtsch. chem. Ges. 45, 262 (1912)];

b) by heating VCl_3 in an O_2-containing N_2 stream;

c) by heating $VOCl_3$ in a pure N_2 stream [P. Ehrlich and H. J. Seifert, Z. anorg allg. Chem. 301, 282 (1959)].

PROPERTIES:

Formula weight 102.41. Brown crystals, the particle size depending on method of preparation. Decomposes at about 600°C into VCl_3 and the oxide; not attacked by H_2O, hydrochloric acid or alkalies; dissolves in warm conc. HNO_3 and conc. H_2SO_4. d 3.44. Rhombic crystals, isotypical with FeOCl.

REFERENCES:

H. Schäfer and F. Wartenpfuhl. J. Less-Common Metals 3, 29 (1961); P. Ehrlich and H. J. Seifert. Z. anorg. allg. Chem. 301, 282 (1959).

Vanadium Oxydichloride

$VOCl_2$

$$\underset{181.9}{V_2O_5} + 3\,\underset{472.0}{VCl_3} + \underset{173.3}{VOCl_3} = 6\,\underset{627.2}{VOCl_2}$$

A thoroughly ground mixture of 3.6 g. of dry V_2O_5 and 9.4 g. of VCl_3 is placed at the closed end of a 1-m.-long tube, and 0.9 ml. of $VOCl_3$ is then added. The upper part of the tube must be free of traces of these substances. The tube, filled with air, is melt-sealed, and is covered along its entire length with a sheet-metal jacket, this

lower third, in a slightly inclined position, is then heated to about 600°C with a tubular electric furnace. The sheet-metal jacket provides a temperature gradient along which the product $VOCl_2$ sublimes out of the hot reaction zone. This procedure requires at least 4–5 days. However, the yield can be increased by longer heating time. Green needlelike crystals of $VOCl_2$ are deposited in the cold part of the tube. The tube is opened at a suitable spot; the product is suspended in petroleum ether, ethyl ether or CCl_4 to dissolve some adhering $VOCl_3$, and then suction-filtered on a coarse fritted-glass filter. The relatively coarse filter separates the $VOCl_2$ crystals from traces of finely divided hydrolysis products. The $VOCl_2$ is freed of adhering solvent and stored under anhydrous conditions.

Alternate method: The older method of reducing $VOCl_3$ with Zn powder in a sealed tube is less efficient (Gmelin–Kraut, Handb. d. anorg. Chem. [Handbook of Inorg. Chem.], 7th Ed., Heidelberg, 1908, Vol. III/2, p. 120).

SYNONYM:

Vanadyl dichloride.

PROPERTIES:

Formula weight 137.86. Shiny green crystals; hygroscopic. d 2.88. Solutions of $VOCl_2$ in aqueous hydrochloric acid are obtained by adding VCl_4 to H_2O or by heating V_2O_5 with excess conc. HCl and evaporating most of the excess HCl. The evolution of Cl_2 brought about in this manner can be greatly facilitated by addition of weak reducing agents such as ethanol or H_2S.

REFERENCE:

H. Funk and W. Weiss, Z. anorg. allg. Chem. 295, 327 (1958).

Vanadium Oxytrichloride

$VOCl_3$

I. $$\underset{181.9}{V_2O_5} + 3\,\underset{356.9}{SOCl_2} = 2\,\underset{345.6}{VOCl_3} + 3\,SO_2$$

A flask connected to a reflux condenser via a ground joint is charged with 20 g. of V_2O_5 and 24 ml. of $SOCl_2$ (equivalent quantities) and heated for 6–8 hours on a water bath under rigorously anhydrous conditions. After rearranging the apparatus for forward distillation, the reaction product is distilled directly from the flask. This method yields pure $VOCl_3$ provided no excess of $SOCl_2$ is used.

II. $$\underset{149.9}{V_2O_3} + \underset{67.2\ l.}{3\,Cl_2} = \underset{346.6}{2\,VOCl_3} + {}^1/_2O_2$$

Pellets, obtained by compressing a mixture of V_2O_3 and coal powder, are heated at 500–600°C in a Cl_2 stream. The red-brown reaction product, containing $VOCl_3$ as well as considerable amounts of VCl_4 and Cl_2, is repeatedly redistilled over Na metal until it is yellow. The product should not be distilled to dryness because it is likely to ignite. Rigorously anhydrous conditions are required.

Alternate method: The VCl_3 is heated in a stream of O_2, using the apparatus described for the preparation of VCl_4 from VCl_3 and Cl_2, p. 1259 [H. Funk and W. Weiss, Z. anorg. allg. Chem. 295, 327 (1958)].

SYNONYM:

Vanadyl trichloride.

PROPERTIES:

Formula weight 173.32. Light-yellow liquid. M.p. −79.5°C, b.p. 127°C; vapor pressure (0°C) 4.4 mm., (80°C) 175 mm.; d (0°C) 1.85, (32°C) 1.81. Instantly hydrolyzed by H_2O; quickly attacked even by atmospheric moisture; violent reaction with Na above 180°C. Soluble in ethanol, ethyl ether and glacial acetic acid.

DropBooks

REFERENCES:

I. H. Hecht, G. Jander and H. Schlapmann, Z. anorg. Chem. 254, 255 (1947).

II. W. Prandtl and B. Bleyer, Z. anorg. Chem. 65, 153 (1909); L. Vanino, Handb. d. präp. Chemie, Anorg. Teil [Handbook of Preparative Chemistry, Inorganic Section], 3rd Ed., Stuttgart, 1925, p. 675; F. E. Brown and F. A. Griffits in: H. S. Booth, Inorg. Syntheses, Vol. I, New York-London, 1939, p. 106 and J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 80; A. Morette, Comptes Rendus Hebd. Séances Acad. Sci. 202, 1846 (1936).

Vanadium Dioxychloride

VO_2Cl

$$\underset{173.3}{VOCl_3} + \underset{86.9}{Cl_2O} = \underset{118.4}{VO_2Cl} + 2\,Cl_2$$

A 250-ml., two-neck flask equipped with a large-diameter inlet tube, with all joints and stopcocks made gas-tight with Hostaflon

(Farbwerke Hoechst) or Teflon grease, is purged with dry N_2. Then pure $VOCl_3$ (100 ml.) is distilled in, and Cl_2O gas diluted with O_2 is introduced at room temperature. The Cl_2O gas mixture is obtained by passing O_2 and Cl_2 (both dried over P_2O_5) over HgO. It is advantageous to keep the HgO in a rotatable glass tube surrounded by a cooling jacket (Liebig condenser).

After a while an orange-colored, microcrystalline mass is formed, while the temperature of the reaction mixture increases slightly. The O_2–Cl_2O feed is continued until the quantity of the crystals formed makes further feeding impossible. The material is filtered under rigorously anhydrous conditions and then vacuum-dried. The product must not be washed with CCl_4, because this solvent slowly reacts with VO_2Cl even at room temperature, affording phosgene.

The yield, based on Cl_2O, is nearly quantitative; based on $VOCl_3$, it is not higher than 60%.

PROPERTIES:

Orange-red, microcrystalline, very hygroscopic powder. At 150°C, disproportionates into V_2O_5 and $VOCl_3$. Sparingly soluble in nonpolar solvents, moderately soluble in ethyl ether, soluble in H_2O with decomposition. d 2.29.

REFERENCE:

K. Dehnicke, Personal communications, 1960.

Lower Vanadium Oxides

V_6O_{13}

$$\underset{363.8}{2\,V_2O_5} + \underset{149.9}{V_2O_3} = \underset{513.7}{V_6O_{13}}$$

a) A stoichiometric mixture of V_2O_5 and V_2O_3 is heated for 48 hours at not less than 600°C, preferably at 750–800°C, in an evacuated, sealed quartz tube.

b) Or, the V_2O_5 surface is reduced in an SO_2 stream at a temperature somewhat higher than 700°C, and the unreacted V_2O_5 is extracted from the reaction product with conc. ammonia.

PROPERTIES:

Blue-black, crystalline powder. Readily soluble in conc. HNO_3, sparingly soluble in conc. ammonia and 2 N NaOH. The independent

phase with a monoclinic crystal structure is stable only below about 700°C.

VO_2

Since the direct reduction of V_2O_5 does not give a well-defined product, this compound is best prepared by synthesis from V_2O_5 and V_2O_3, suggested a long time ago by Berzelius:

$$\underset{181.9}{V_2O_5} + \underset{149.9}{V_2O_3} = \underset{331.8}{4\,VO_2}$$

An intimate mixture of V_2O_5 and V_2O_3, in the exact proportion required by the equation, is heated for 40–60 hours at 750–800°C in a small evacuated, sealed quartz tube.

Alternate methods: The V_2O_5 is fused with an excess of crystalline oxalic acid until a greenish-blue, completely water-soluble mass of vanadyl oxalate is obtained. This mass is then calcined to complete decomposition in the absence of air. The VO_2 is obtained as the residue.

PROPERTIES:

Blue-black powder. M.p. 1650°C; d 4.34. Deformed C 4 (rutile) type crystal structure.

DropBooks

V_nO_{2n-1}

According to G. Anderson, several lower vanadium oxides have very similar compositions which are intermediate between those of VO_2 and of V_2O_3 and correspond to the formula V_nO_{2n-1} (where n = 3, 4, 5, 6, 7 or 8). These oxides have very narrow regions of homogeneity and are obtained by vacuum heating corresponding mixtures of V_2O_5, V_2O_3 and V for 2–20 days at 650–1000°C.

V_2O_3

$$\underset{181.9}{V_2O_5} + \underset{44.8\,l.}{2\,H_2} = \underset{149.9}{V_2O_3} + \underset{36.0}{2\,H_2O}$$

The V_2O_5 is reduced in a stream of very pure H_2 in two steps: first, for 2 hours at 600°C (the 658°C m.p. of V_2O_5 should not be exceeded), then for 6 additional hours at 900–1000°C.

For information on the formation of V_2O_3 single crystals, see H. Hahn and C. de Laurent, Angew. Chem. 68, 523 (1956).

PROPERTIES:

Dull, black powder. M.p. 1970°C; d 4.87. Crystal structure: alumina type.

VO

$$\underset{149.9}{V_2O_3} + \underset{51.0}{V} = 3\,\underset{200.9}{VO}$$

Synthesized from V_2O_3 and V metal powder under vacuum or Ar. The reactants are kept in Al_2O_3 crucibles which, in turn, are inserted into small, evacuated quartz tubes. Or, the apparatus described by Ehrlich for the preparation of TiO (p. 1214) may be used. The optimum reaction temperatures lie between 1200 and 1600°C. A product of greater uniformity is obtained by occasionally interrupting the heating and repulverizing the material. A reaction time of the order of 24 hours at 1200–1300°C is needed, whereas 1 hour is sufficient at 1600°C.

Alternate method: Electrolysis of phosphate melts containing dissolved V_2O_5 [H. Hartmann and W. Mässing, Z. anorg. allg. Chem. 266, 98 (1951)].

PROPERTIES:

Gray powder. The region of homogeneity is $VO_{0.75}$–$VO_{1.20}$. Crystal structure: B 1 (NaCl) type.

REFERENCES:

H. Fendius, Thesis, Univ. of Hannover, 1930; W. Klemm and L. Grimm, Z. anorg. allg. Chem. 226, 359 (1936); W. Klemm and E. Hoschek, Z. anorg. allg. Chem. 242, 63 (1939); W. Klemm and L. Grimm, Z. anorg. allg. Chem. 250, 42 (1942); W. Klemm and P. Pirscher, Optik 3, 75 (1948); F. Aebi, Helv. Chim. Acta 31, 8 (1948); S. S. Todd and K. R. Bonnickson, J. Amer. Chem. Soc. 73, 3894 (1951); M. Frandsen, J. Amer. Chem. Soc. 74, 5046 (1952); N. Schönberg, Acta Chem. Scand. 8, 221 (1954); G. Anderson, Acta Chem. Scand. 8, 1509 (1954).

Vanadium (III) Hydroxide

$V(OH)_3$

A neutral Na_3VO_4 solution is reduced electrolytically at a mercury cathode.

A) PREPARATION OF THE VANADATE SOLUTION

$$\underset{181.9}{V_2O_5} + \underset{240.0}{6\,NaOH} = \underset{367.9}{2\,Na_3VO_4} + \underset{54.0}{3\,H_2O}$$

Concentrated NaOH is prepared from equal weights of NaOH and H_2O, and the solution is filtered in the absence of CO_2 to remove the Na_2CO_3 contaminant. The strength of the solution is then determined by analysis. The amount of V_2O_5 required by the above equation is then dissolved in this solution, and 1 M Na_3VO_4 is prepared by dilution with water.

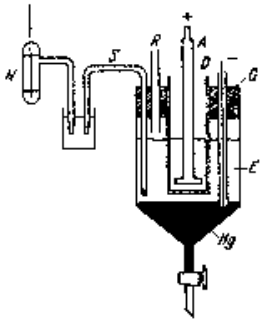

Fig. 302. Preparation of vanadium (III) hydroxide. A) carbon anode; D) clay diaphragm; E) electrolyte solution; C) rubber stopper; N) standard cell; R) N_2 inlet type; S) electrolyte bridge.

B) ELECTROLYSIS

An electrolysis cell of the type shown in Fig. 302 is filled with very pure Hg and the Na_3VO_4 solution. The cell is closed off with rubber stopper C, and the anode space within the clay diaphragm D is filled with 1 M Na_2SO_4 solution. Very pure N_2 is bubbled (via inlet tube R) through the electrolyte solution for the first 15 minutes, and is passed over the liquid surface for the remainder of the electrolysis. Electrolysis is carried out with a current of 0.1 amp. at a cathode potential of −1.70 v. (checked by means of the standard cell N). Brown-green $V(OH)_3$ precipitates, and the electrolyte assumes a brown-red color. The electrolysis is discontinued after 5–10 hours, and $V(OH)_3$ isolated in the absence of air. This is accomplished by first draining the Hg through the stopcock, then suction-filtering the $V(OH)_3$ suspension under a N_2 atmosphere and thoroughly washing the precipitate with deaerated H_2O. Finally the $V(OH)_3$ is dried in high vacuum.

PROPERTIES:

Formula weight 101.97. Brass-colored, crystalline; readily oxidized by O_2.

REFERENCE:

N. Konopik and A. Neckel. Monatsh. Chem. 88, 917 (1957).

Vanadium (V) Oxide

V_2O_5

Highest grade V_2O_5 is obtained by calcining NH_4VO_3 at 500–550°C. Traces of N usually contaminating the product thus obtained can be virtually eliminated by heating for 18 hours at 530–570°C in a moist O_2 stream.

PROPERTIES:

Formula weight 181.9. Red to orange-yellow powder. M.p. 674°C. Slightly soluble in water: 0.07 g./100 g. H_2O; d 3.36. Readily soluble in alkali hydroxide solutions, acids and ethanol. Crystal structure: orthorhombic.

Supported V_2O_5 (V_2O_5 catalysts)

I. ON ASBESTOS

A solution of 5 g. of NH_4VO_3 in 100 ml. of boiling H_2O is reduced with NH_4HSO_3 and treated with sulfuric acid until the solution turns a pure blue-violet. Asbestos (20 g.) is added; the mixture is allowed to boil for 10–15 minutes and is then cooled to 40–50°C; it is then rendered strongly alkaline by addition of conc. NH_3, whereby the $V(OH)_3$ precipitates onto the asbestos. The latter is dried and again treated with unreduced NH_4VO_3, whereupon the asbestos and the flask wall become violet-blue. The asbestos mass is then pulled apart into small clumps, dried and calcined at 500–600°C; its V_2O_5 content may be as high as 50%.

II. ON CERAMIC MATERIALS

To produce a homogeneous deposit of V_2O_5 on ceramic materials (e.g., firebrick), 2–3 equivalents of a mineral acid is added to a NH_4VO_3 solution. The resulting dark-yellow solution, which contains colloidal $V_2O_5 \cdot aq.$, is boiled in the presence of the ceramic material (heating on the water bath is insufficient), thereby causing precipitation onto the carrier of a yellow-red, strongly adhering layer of V_2O_5. Glass (not porcelain) reaction vessels should be used in this process.

REFERENCES:

N. Yefremov and A. Rozenberg. Khim. Prom. 4, 129; Chem. Zentr. 1927, II, 1994; I. Adadurov and G. Boreskov. Khim. Prom. 6, 732; Chem. Zentr. 1929, II, 2926.

Colloidal V_2O_5

I. METHOD OF BILTZ

a) A mortar is used to grind 1 g. of NH_4VO_3 with some H_2O, and 10 ml. of 2 N HCl is added while stirring with the pestle. The red precipitate formed and the supernatant are transferred onto a filter, the liquid is filtered off, and the solid is washed with H_2O. After a while, the initially clear filtrate becomes reddish and turbid. The precipitate is then transferred from the filter to an Erlenmeyer flask (using water from a wash bottle), and the volume is adjusted to 100 ml. The quantities of material used may be increased up to 200-fold, provided the proportions are kept the same. After a few hours the conversion of the precipitate to a clear orange-red V_2O_5 sol is complete. Fibrillar birefringence becomes evident only after prolonged standing.

b) In the modification of Humphry, 0.5 g. of NH_4VO_3 and 2 ml. of nitric acid (1 vol. of conc. HNO_3 + 10 vol. of H_2O) are ground together and then an additional 2 ml. of HNO_3 is added. The mixture is filtered, and the V_2O_5 formed is washed until it starts passing through the filter; it is then shaken with 200 ml. of H_2O and allowed to stand for 14 days.

PROPERTIES:

Because of the fibrillar structure of the particles, the sol exhibits strong streaming birefringence and on aging shows an increase in fibril length. Part of the V_2O_5 is always molecularly dissolved, in an amount increasing symbatically with the total concentration. The sol absorbs electrolytes strongly, and always contains some vanadium (IV).

DropBooks

II. METHOD OF PRANDTL AND HESS: SAPONIFICATION OF TERT-BUTYL ORTHOVANADATE

$$\underset{572.8}{2\,(C_4H_9)_3VO_4} + \underset{54.0}{3\,H_2O} = \underset{181.9}{V_2O_5} + \underset{444.7}{6\,C_4H_9OH}$$

a) *tert*-Butyl alcohol and V_2O_5 are refluxed for several hours, affording a light-yellow solution of *tert*-butyl orthovanadate containing 5.3 g. of V_2O_5 per 100 g. The solution is filtered and subjected to fractional vacuum distillation in an Anshütz flask. This ester is sometimes repurified by a second vacuum distillation. Ester properties: b.p. 117°C (15 mm.), 132°C (32 mm.); m.p. 45-47°C.

b) H_2O is added to the ester; this produces a very loose (swollen) orange-colored precipitate. On boiling with a large quantity of H_2O, a clear, colloidal V_2O_5 solution is obtained. The alcohol (b.p. 82°C) is completely eliminated by the boiling.

PROPERTIES:

Electrolyte-free, virtually monodisperse sol; does not age appreciably.

Alternate methods: a) Pouring molten V_2O_5 into H_2O gives a fairly polydisperse sol, which is electrolyte-free and undergoes little or no aging [E. Müller, Kolloid-Z. 8, 302 (1911)].

b) Dissolving V_2O_5 in dilute H_2O_2 and boiling the solution affords a strongly polydisperse sol, which is electrolyte-free and does not age appreciably [W. Ostermann, Jahrb. d. philos. Fak. Göttingen II, 265 (1921)].

REFERENCES:

General: H. Gessner. Kolloid-Beih. 19, 213 (1924).

I. W. Biltz, Ber. dtsch. chem. Ges. 37, 1095 (1904); E. Sauer, Kolloidchem. Praktikum [Lab. Manual of Colloid Chemistry], Berlin, 1935; R. H. Humphry, Proc. Phys. Soc. (London) 35, 217 (1923).

II. W. Prandtl and L. Hess, Z. anorg. allg. Chem. 82, 102 (1913).

Ammonium Metavanadate

NH_4VO_3

Ammonium metavanadate is a common commercial product, but its purity usually leaves something to be desired. Since it is easily prepared from V_2O_5 (see method II) and in turn readily yields V_2O_5 on calcination, it plays an important role in the preparation and purification of vanadium compounds. Only the purification of NH_4VO_3 is treated here.

I. A saturated NH_4VO_3 solution is prepared in boiling, weakly ammoniacal H_2O. About 500 ml. of H_2O is required for 25 g. of NH_4VO_3 but, to avoid excessive hydrolysis, it is better to use more water than to prolong the boiling. The solution is filtered hot through a fine-pore fritted glass filter, 10% of its weight of solid NH_4Cl is added to the filtrate, and the mixture is cooled to 0°C. The precipitating NH_4VO_3 is allowed to stand at 0°C (1 hour); it is then suction-filtered and washed with a small amount of ice-cold, ammoniacal H_2O and finally with some ice-cold pure water.

If necessary, this recrystallization may be repeated several times. Complete removal of alkali ions and traces of $V_2O_5 \cdot xH_2O$ (formed on slight hydrolysis) is extremely difficult.

II. If a smaller volume of liquid is desired, V_2O_5 is dissolved in Na_2CO_3 as $NaVO_3$, and NH_4VO_3 is precipitated from this solution by addition of NH_4Cl.

Thus 25 g. of V_2O_5 is added, in small portions and with stirring, to a boiling solution of 17.5 g. of anhydrous Na_2CO_3 in 125 ml. of H_2O. After the CO_2 evolution has subsided, saturated $KMnO_4$

solution is added to the reaction mixture in an amount just sufficient to discharge the green-blue color stemming from partial reduction of the vanadium. Undissolved V_2O_5 and MnO_2 are carefully suction-filtered on a fine-pore fritted glass filter until the filtrate is completely clear. The residue is washed with H_2O until H_2O_2 no longer gives a positive reaction for vanadium. The filtrate, which amounts to about 125–150 ml., is heated to 60°C and then poured all at once into a hot solution of 75 g. of NH_4Cl in 125 ml. of H_2O. Precipitation of NH_4VO_3 starts immediately and is complete after a few hours. Some of the salt adheres fairly tenaciously to the glass walls. The salt is suction-filtered and washed with small portions of H_2O until the washings are free of chloride ion. It is then dried in air at a temperature below 40°C. An almost pure-white salt, still containing some Na (about 0.3% NaCl) is obtained in 80% yield.

The NH_4VO_3 can be recrystallized under similar conditions. For example, 25 g. of the salt is dissolved in a solution of 16 g. of Na_2CO_3 in 125 ml. of H_2O with mild heating (to 30–40°C). The mixture is then carefully filtered and precipitated at once with NH_4Cl as described above.

PROPERTIES:

White, crystalline salt, often yellowish due to slight traces of V_2O_5. Solubility: (15°C) 0.52 g., (32°C) 1.0 g., (50°C) 1.6 g. per 100 g. of H_2O. d 2.33. Liberates NH_3 above 50°C. Readily converted to V_2O_5 when heated dry.

PrepBooks

REFERENCES:

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II. R. H. Baker, H. Zimmermann and R. N. Maxson in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York–Toronto–London, 1950, p. 117; experimental data and personal communications from several laboratories.

Alkali Vanadates

Among the alkali vanadates, only $NaVO_3$ is commercially available. However, the number of existing defined alkali vanadates is rather large. Only the system K_2O–V_2O_5 has been subjected to a systematic preparative study. It may be assumed that the other systems have similar structures.

A stoichiometric mixture of K_2CO_3 and V_2O_5 (for example, a total of 5–6 g.) is heated in an open crucible. The crucible material

is Pt or, if the mixtures are rich in alkali, an 80% Au–20% Pd alloy. The temperature should not be increased at a rate faster than 10°C/min., in order to prevent a too vigorous reaction which would result in loss by spattering. At low alkali contents, the maximum required temperature is about 500°C, while 1000°C is needed when the alkali content is high. Several hours (8–24) of heating are required at these temperatures. The product is cooled to below 350°C in a desiccator to prevent moisture absorption. The preparation must be modified somewhat, depending on raw material composition (see the original literature).

The phase diagram of the K_2O–V_2O_5 system shows the existence of the following potassium vanadates: $K_2O \cdot 4\ V_2O_5$ (m.p. 520°C, incongruent); $K_2O \cdot V_2O_5$ (m.p. 520°C); $16\ K_2O \cdot 9\ V_2O_5$ (m.p. 696°C, incongruent); $2\ K_2O \cdot V_2O_5$ (m.p. 910°C); $3\ K_2O \cdot V_2O_5$ (m.p. ~ 1300°C).

REFERENCE:

F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, J. Amer. Chem. Soc. 78, 1536 (1956).

Vanadium Sulfides

All vanadium sulfides can be synthesized from the elements. An intimate mixture of the finely pulverized components, in the proper proportions, is placed in sintered clay tubular crucibles; these are inserted in quartz tubes, which are then evacuated and melt-sealed. The tubes are then slowly heated and finally maintained for a long time at a maximum temperature of 1000–1300°C. Contact between the vanadium metal and the quartz must definitely be avoided.

This procedure yields V_3S, VS and V_2S_3.

$3\,V$	$+\ S$	$=\ V_3S$;	V	$+\ S$	$=\ VS$;	$2\,V$	$+\ 3\,S$	$=\ V_2S_3$
152.9	32.1	185.0	50.9	32.1	82.1	101.9	96.2	198.1

All the sulfides, as phases of the V–S system, have more or less wide regions of homogeneity.

Other preparative methods can also be used to obtain particular sulfide phases.

VS

$$\underset{198.1}{V_2S_3} = \underset{166.0}{2\,VS} + \underset{32.1}{S}$$

Thermal decomposition of V_2S_3 at 1000°C in a H_2 stream yields a product of composition $VS_{1.03}$ in 20 hours.

Pure VS can also be prepared by prolonged calcination of V_2O_5 in a stream of H_2S.

PROPERTIES:

VS exists, as a phase of the V–S system, between $VS_{1.00}$ and $VS_{1.18}$. d 4.51. It has a B8 (NiAs) type crystal structure with voids.

V_2S_3

$$\underset{149.9}{V_2O_3} + 3\,\underset{102.2}{H_2S} = \underset{198.1}{V_2S_3} + 3\,\underset{54.0}{H_2O}$$

A thin layer of about 0.5 g. of V_2O_3 is spread in a porcelain boat, which is then inserted into a suitable tube and heated for 10 hours at 750°C in a moderately fast H_2S stream, predried over silica gel. At the end of this heating period, the tube is cooled in an H_2S stream and the V_2S_3 removed from the boat. A uniform and thin layer of V_2O_3 is essential to achieve a reasonable reaction time. Under the same conditions, 2–3 g. of V_2O_3 requires 2 days for complete conversion to the sulfide. Increasing the temperature to 850°C reduces the reaction time to a few hours, but the end product contains somewhat less S than required by the formula V_2S_3 (e.g., $VS_{1.47}$).

In addition, V_2O_5 can also be used as the starting material, by heating it at 700°C in a stream of CS_2 vapor. For data concerning the formation of V_2S_3 single crystals, see H. Hahn and C. de Laurent, Angew. Chem. 68, 523 (1956).

PROPERTIES:

Homogeneous between $VS_{1.17}$ and $V_{1.53}$. Dark-gray powder. Quite resistant to dil. acids; in contrast to VS_4, insoluble in dilute sodium hydroxide. d 3.7.

VS_4

A mixture of V_2S_3 and excess S, corresponding to the approximate formula VS_{20}, is heated for 15 hours at 400°C in a sealed tube, followed by a 12-hour annealing period at 90°C (to convert the excess S into the soluble α-form). The reaction product is then exhaustively extracted in a Soxhlet apparatus, with the VS_4 remaining as the residue. Extending the heating period (to several months) affords larger crystals.

PROPERTIES:

Formula weight 179.19. Black powder. Composition sometimes does not correspond exactly to the formula. Unstable above 500°C, decomposing into V_2S_3 and S. Quite resistant to dilute acids; readily and completely soluble in sodium hydroxide, yielding a red solution. $VS_{3.65}$: d 2.8.

REFERENCES (all sulfides):

W. Biltz and A. Köcher. Z. anorg. allg. Chem. 241, 324 (1939); E. Hoschek and W. Klemm. Z. anorg. allg. Chem. 242, 49 (1939); W. Klemm and E. Hoschek. Z. anorg. allg. Chem. 226, 362 (1936); B. Pedersen and F. Grønvold. Acta Crystallogr. 12, 1022 (1959); B. Pedersen. Acta Chem. Scand. 13, 1050 (1959); G. M. Loginov. Zh. Neorg. Khimii 5, 221 (1960).

Vanadium Selenides

I. $V_2O_3 + 3H_2 + 3Se = V_2Se_3 + 3H_2O$

149.9 67.2 l. 236.9 338.8 54.0

About 0.5 g. of V_2O_3, which during its preparation has been heated not higher than 500–600°C so that is an active product capable of fast reaction, is placed in a small porcelain boat, which is inserted into a quartz tube. A larger boat containing Se is placed ahead of the one containing V_2O_3, and a stream of very pure H_2 is passed through the tube. The V_2O_3 zone is first heated to 600°C, and then gradually to 900°C, using a small tubular electric furnace; simultaneously, the Se is vaporized by heating with a gas burner. The section of the quartz tube extending beyond the furnace is cooled with a cooling coil. After passing over the reaction product, most of the Se condenses in this section. After the reaction, the tube is allowed to cool and the product is repulverized; the selenation is repeated twice.

The composition of the products thus obtained varies markedly: when prepared at 800°C, the end product is $\sim VSe_{1.9}$, at 1000°C $\sim VSe_{1.4}$.

II. Heating the above products with a suitable excess of Se in a short sealed quartz tube at a temperature which, depending on the Se content, should be between 600 and 800°C affords products with a higher Se content.

III. Thermal degradation of the products of the first selenation, by heating in a high vacuum at 1000–1100°C for several days, affords $VSe_{1.0}$.

PROPERTIES:

The V–Se system has 3 stable phases with very broad homogeneity regions.

α-Phase (VSe), from $VSe_{1.0}$ to $VSe_{1.26}$. Dull-gray powder. d 5.94. B8 (NiAs) type crystal structure, with voids.

β-Phase (V_2Se_3), from $VSe_{1.25}$ to $VSe_{1.30}$. Gray powder with metallic luster. d 5.87.

γ-Phase (VSe_2), from $VSe_{1.62}$ to $VSe_{1.67}$. Gray, small, leaf-like crystals with metallic luster. d 5.79. Crystal structure: C6 (CdI_2) type.

REFERENCE:

E. Hoschek and W. Klemm. Z. anorg. allg. Chem. 242, 49 (1939).

Vanadium (II) Sulfate

$VSO_4 \cdot 6\,H_2O$

Produced by electrolytic reduction of $VOSO_4$, followed by ethanol precipitation of $VOSO_4 \cdot 6\,H_2O$ from the resulting vanadium (II) solution.

$$\underset{217.1}{VOSO_4 \cdot 3\,H_2O} \rightarrow \underset{255.1}{VSO_4 \cdot 6\,H_2O}$$

DropBooks

A) ELECTROLYTIC REDUCTION

The electrolysis vessel consists of a glass cylinder, 5 cm. in diameter and 10 cm. high, such as, for example, a small Pyrex pressure vessel. This vessel is closed with a five-hole rubber stopper to accommodate the cathode stem, thermometer, diaphragm, and N_2 inlet and outlet tubes. A suitable outlet tube is a small fermentation tube, which serves as protection against air and should, if possible, be drawn out into an outward-pointing capillary.

The cathode is made by bending a lead strip (3 × 25 × 80 mm.) into a cylinder so that it encloses the diaphragm. A hole is then drilled near one end of the Pb strip, and a lead rod (serving as a bus bar) is attached to it by hammering in place. The anode also consists of a lead rod, which can be prepared by pouring molten Pb into a glass tube, while cautiously fanning the latter with a flame, and then cooling and breaking the tube. Prior to electrolytic reduction, the cathode is pretreated, according to the method of Tafel, by using the cathode as an anode in 2N H_2SO_4 until it is uniformly coated with brown PbO_2. The diaphragm consists of a glass tube, about 16 cm. long and 2 cm. I.D., with a fine fritted-glass disk sealed to its lower end.

A 2M $VOSO_4$ solution, which is also 2N in H_2SO_4, is prepared by dissolving 66 g. of $VOSO_4 \cdot 3\,H_2O$ (for preparation, see p. 1285) in H_2O, adding 8.5 ml. (15 g.) of conc. H_2SO_4, and diluting to 150 ml. with H_2O.

The diaphragm is filled with 6N H_2SO_4 to the level of the $VOSO_4$ solution in the cathode space. This is best done by pouring both solutions in at the same time. Electrolysis is started at 0.3 amp. and about 5 v. Cooling is unnecessary, since the temperature does not exceed 30°C. If the current should exceed 0.3 amp. during the first few hours, it must be readjusted to this value. During the intermediate reduction period, the current drops to 0.2 amp., while the voltage increases. The current should, however, not be raised to 0.3 amp. During reduction, the dark-blue $VOSO_4$ solution first turns dark blue-green, then later dark and opaque. In the final reduction period the current again rises while the voltage drops. Reduction is complete when the solution is red-violet. Reduction time: 55-60 hours. During electrolysis, a slow stream of O_2-free N_2 or CO_2 is passed through the electrolyte at the cathode.

If only the reduced vanadium (II) solution is needed and precipitation of crystalline VSO_4 is not desired, the electrolyte solution can be protected from atmospheric O_2 in a simpler fashion, by covering it with a xylene layer about 2 cm. deep.

If desired, the electrolysis may be continued at 0.01-0.02 amp. and 3 v. for several months; a completely reduced VSO_4 solution is thus always available for use. To remove solution as needed, the gas outlet tube is pulled out of the rubber stopper and a pipette inserted in its place. Virtually no oxidation takes place if the VSO_4 solution aspirated into the pipette is immediately allowed to run out into another vessel under an inert gas blanket.

A low current density is necessary in order to obtain a relatively concentrated VSO_4 solution with a minimum H_2SO_4 content, as required for the precipitation with ethanol described below.

B) PRECIPITATION WITH ABSOLUTE ETHANOL

The glass apparatus shown in Fig. 303 is suitable for the isolation of crystalline VSO_4. Its main section is adapter *k*, bent at an angle of about 100°. The ends of *k* are connected via standard taper joints to the other parts of the apparatus. The joints are lightly lubricated with stopcock grease. The entire apparatus is fastened to a cross-shaped supporting rack of iron bars by means of two common clamps (not shown in the drawing), one holding the neck of the round-bottom flask *p* and the other the receiver *m*. The rack can be rotated, with moderate resistance, about its axis (which is perpendicular to the plane of the drawing).

The gas inlet tube *e* is connected via a pressure hose to a two-way stopcock which connects the system either to an oil-type

vacuum pump or to a source of pure, P_2O_5-dried N_2. The N_2 must be very pure; it is pressurized to 0.2 atm. gauge by means of a Hg or H_2O leveling device (2-m. water column), and then introduced into the apparatus. A two-liter flask, serving as a N_2 surge vessel, is inserted between the N_2 purifier and the P_2O_5 drying train.

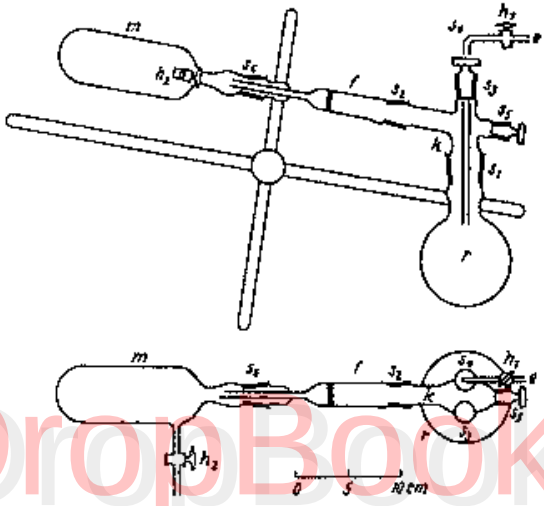

Fig. 303. Preparation of vanadium (II) sulfate. *k*) bent adapter; s_1) 29/26 joint; s_2) 24/25 joint; s_3 and s_4) 12/18 joints; *e*) gas inlet tube with stopcock h_1; *r*) 250-ml. round-bottom flask; *f*) tubular adapter with fritted-glass disk; *m*) receiver; h_1 and h_2) stopcocks.

The apparatus is completely purged of air by alternate evacuation and flushing with nitrogen. Then 20 ml. of 2 M VSO_4 solution is removed from the electrolysis vessel with a pipette, the stopper s_3 is removed, the pipette is immediately inserted through this opening until it almost touches the bottom of flask *r*, and the solution is allowed to flow out. With stopcock h_1 open, the filling operation is carried out in a countercurrent nitrogen stream.

In the same manner 40 ml. of absolute ethanol, previously deaerated by boiling while passing through pure dry nitrogen, is added to flask *r*. Stopper s_3 is immediately closed, and the entire apparatus vigorously shaken for 5 minutes by a back-and-forth movement of the cross arm. Solid, granular $VSO_4 \cdot 6\ H_2O$ begins to precipitate within a few seconds. Stopcock h_2 is now connected

via a rubber hose to a wash bottle containing some water and also serving as a bubble counter and liquid seal. With stopcocks h_1 and h_2 open, the pale-purple mother liquor is decanted by carefully tilting the cross arm. The salt precipitate in r is washed by vigorous shaking with the liquid quantities indicated below and decanting the used liquid before each new addition. The wash liquid is introduced, as indicated above in the case of the VSO_4 solution, in a countercurrent N_2 stream by means of a pipette inserted through s_3. The wash liquids are introduced in the following order: 2×15 ml. of deaerated absolute ethanol; 25 ml. of the same ethanol plus 10 ml. of absolute ether; 10 ml. of ethanol plus 25 ml. of ether; 5 ml. of ethanol plus 15 ml. of ether; 3 ml. of ethanol plus 25 ml. of ether. Finally the salt is transferred onto the fritted-glass filter f with an additional 25 ml. of absolute ethyl ether. The ether adhering to the substance is removed by continuing the N_2 purge stream (about one hour). Flask m is replaced with the N_2-filled drying vessel t shown in Fig. 304 while continuing the N_2 stream via h_3. Vessel t is charged to one third of its capacity with a P_2O_5-pumice drying mixture, and any oxygen present in the latter is removed by alternate evacuation and purging with N_2. Then the drying vessel and the tube f are detached from adapter k at joint s_2, f is immediately closed off with a ground stopper, and the system is connected to the oil vacuum pump by way of h_3 (resetting the two-way stopcock). After evacuation, stopcock h_3 is closed and the drying vessel with the product is allowed to stand for 5 days at 25 °C (drying can also be accomplished, without the P_2O_5-pumice mixture, by immersing the evacuated drying vessel in liquid nitrogen). The light red-violet product is stored in container n, shown in Fig. 304, which provides protection from oxygen and enables one to remove the product when desired. To transfer the product to n, the latter is evacuated, then filled with N_2; the drying vessel is also filled with N_2 through h_3, the glass stopper is removed from f, and the storage container n (which carries a male joint), from which the two-joint adapter and bent tube p have just been removed, is inserted in its place. During this operation, the N_2 stream is introduced via stopcock h_4 of the storage container, as well as via h_3. The substance is transferred to n from the fritted-glass tube f by turning the tube upside down. The storage container is then detached from the tube and closed off with the two-joint adapter and bent tube p. To remove any O_2 entrained during the transfer, container n is immediately evacuated and filled with N_2; these two operations are then repeated twice. Approximately 10 g. of $VSO_4 \cdot 6\ H_2O$ is obtained (90% yield, based on the 20 ml. of 2 M VSO_4 solution used).

Short exposure of the product to air does not affect its storage stability provided the last traces of O_2 are removed by repeated

purging of the system with N_2. The product is stable for several months, even if frequently sampled.

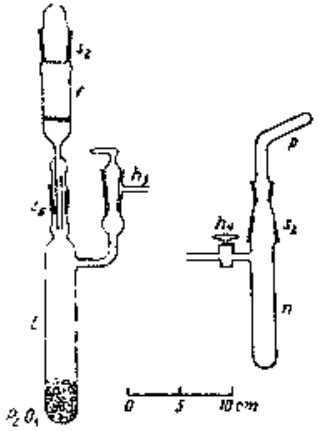

Fig. 304. Drying tube and storage container for vanadium (II) sulfate. *f*) fritted-glass tube as in Fig. 303; *t*) drying tube containing the P_2O_5-pumice mixture; *n*) storage tube *p*) bent tube for filling operations involving small amounts of substance; s_2 and s_3) standard taper joints, as in Fig. 303.

To remove some product from the storage container, the estimated amount is transferred to the bent tube *p* by inclining and tapping *n* (Fig. 304). Nitrogen is introduced via h_4, and tube *p* containing the product is quickly replaced by an identical empty tube. The closed-off storage container is then evacuated twice and filled with N_2; at the same time, the open, previously tared bent tube *p* containing the $VSO_4 \cdot 6\ H_2O$ is quickly weighed (to ascertain the weight of sample in it), and is then quickly connected to the N_2-filled apparatus (Fig. 303) by inserting its male joint into joint s_3. By quickly turning the cross arm, the salt is poured from the bent tube *p* into the flask *r*, whereupon the system (of Fig. 303) is reevacuated via h_1 and refilled with N_2. The $VSO_4 \cdot 6\ H_2O$ can then again be dissolved in O_2-free H_2O, added from a pipette in a countercurrent stream of N_2. In this manner, an H_2SO_4-free solution of VSO_4 is obtained; this can be used to prepare other vanadium (II) compounds in the same apparatus while retaining the certainty that air is completely absent.

Alternate method: A solution of VO in H_2SO_4 is prepared in the absence of air, and is then evaporated in vacuum [C. M. French and J. P. Howard, Trans. Faraday Soc. 52, 712 (1956)].

PROPERTIES:

Light red-violet, fine crystalline powder, oxidized to brown even in dry air. Readily soluble in deaerated H_2O, yielding a red-violet solution.

A heptahydrate $VSO_4 \cdot 7\ H_2O$ may also be formed under other conditions.

REFERENCES:

J. Dehnert. Thesis, Univ. of Jena, 1952 S. Herzog. Z. anorg. allg. Chem. 294, 155 (1958); L. Malatesta. Gazz. Chim. Ital. 71, 615 (1941); J. Meyer and M. Aulich. Z. anorg. allg. Chem. 194, 278 (1930); A. Piccini and L. Marino. Z. anorg. Chem. 50, 49 (1906).

Hydrogen Disulfatovanadate (III)

$$HV(SO_4)_2 \cdot 4\ H_2O$$

A paste obtained by stirring 10 g. of V_2O_5 and 36 g. of conc. H_2SO_4 is heated for a while on a water bath and allowed to stand until the next day. The mixture is then treated with 80 ml. of H_2O and reduced on the water bath by bubbling through it a stream of SO_2. Reduction to $VOSO_4$ is complete in a few minutes. Excess SO_2 is boiled off and the product electrolytically reduced to the trivalent state, using the apparatus described for ammonium vanadium (III) alum (p. 1284). The resulting green solution is filtered on a fine-pore fritted-glass disk and allowed to stand in a vacuum desiccator over H_2SO_4. After a few days, a green crystalline powder separates out; it is stirred with a large quantity of ethanol, suction-filtered and then thoroughly washed with ethanol. The product is dried over H_2SO_4 in a CO_2-filled desiccator.

SYNONYM:

Disulfatovanadic (III) acid.

PROPERTIES:

Formula weight 316.14. Green crystalline powder; can be stored for extended periods of time in closed bottles even in the presence of air.

Other compounds: The above procedure yields $NH_4V(SO_4)_2 \cdot 4\ H_2O$ when 12 g. of NH_4VO_3 is used in place of 10 g. of V_2O_5.

The hexahydrate, $HV(SO_4)_2 \cdot 6\ H_2O$, is formed if 150 g. of H_2SO_4 is used; the salt $NH_4V(SO_4)_2 \cdot 6\ H_2O$ results when NH_4VO_3 is reacted with the stoichiometric amount of H_2SO_4.

Sulfates of trivalent vanadium can be obtained using hydrazine as the reducing agent and glacial acetic acid as the reaction medium. An intermediate, $V(CH_3COO)_3$, is formed under these conditions. Hydrates of $V_2(SO_4)_3$, for example, $V_2(SO_4)_3 \cdot 9\ H_2O$, can be prepared in this manner.

The anhydrous compounds $HV(SO_4)_2$ and $V_2(SO_4)_3$ can be prepared by using conc. H_2SO_4, or by thermal dehydration. See Meyer and Markowicz.

REFERENCES:

J. Meyer and E. Markowicz, Z. anorg. allg. Chem. 157, 211 (1926); J. T. Brierley, J. Chem. Soc. 49, 823 (1886); A. Stähler and H. Wirthwein, Ber. dtsch. chem. Ges. 38, 3970 (1905); J. Dehnert, Personal communication, 1951.

Ammonium and Potassium Disulfatovanadate (III)

$NH_4V(SO_4)_2$, $KV(SO_4)_2$

$NH_4V(SO_4)_2$

A paste prepared by stirring 12 g. of NH_4VO_3 with some H_2O is slowly added to 300 ml. of 2 N H_2SO_4. The resulting pure yellow solution is mixed with 200 ml. of saturated SO_2 solution and 40 g. of $(NH_4)_2SO_4$. The blue solution obtained is evaporated, first on a water bath, then over an open flame, until a blue salt begins to precipitate. Concentrated H_2SO_4 (30–50 ml.) is added and the heating, during which fumes are evolved, continued for a while. The mixture is allowed to cool overnight and is then taken up in H_2O. The residue is suction-filtered, triturated with H_2O, reboiled with H_2O, thoroughly washed, and then dried over H_2SO_4 in a vacuum desiccator. Yield: 4.7 g. of $NH_4V(SO_4)_2$.

$KV(SO_4)_2$

The K salt is prepared similarly, by evaporating a mixture of 200 ml. of 2 N H_2SO_4, 10 g. of vanadyl sulfate, 21.1 g. of K_2SO_4 and 10 ml. of sulfurous acid on a water bath, then adding 10 ml. of conc. H_2SO_4 and heating for a while, while fumes are evolved. After cooling, 400 ml. of H_2O is added and the mixture boiled for a short time. The green product is washed with H_2O, suction-filtered and vacuum-dried over H_2SO_4.

PROPERTIES:

Green, crystalline powder. Insoluble in H_2O and acids; attacked and decomposed by alkali.

REFERENCES:

A. Sievers and E. L. Müller, Z. anorg. allg. Chem. 173, 313 (1928); A. Rosenheim and H. Y. Mong, Z. anorg. allg. Chem. 148, 25 (1925); V. Auger, Comptes Rendus Hebd. Séances Acad. Sci. 173, 306 (1921).

$NH_4V(SO_4)_2 \cdot 12\,H_2O$ (Alum)

A mixture of 25 g. of NH_4VO_3, 180 ml. of H_2O and *a* g. of conc. H_2SO_4 (see below) is prepared with stirring. The hot mixture is treated with SO_2 until a clear, dark-blue $VOSO_4$ solution is formed. Excess SO_2 is boiled off; the mixture is evaporated to 120 ml. and filtered. A porous clay cylinder 5 cm. in diameter and 10 cm. high, serving as diaphragm, is placed in a Pt cup (12 cm. in diameter and 6 cm. high). The vanadium salt solution is poured into the annular space; then, 25 ml. of 10% H_2SO_4 and a Pt coil serving as anode are placed in the inner space, and the mixture is subjected to electrolysis for 45–50 min. at 3–4 v. and 6–7 amp. The electrolysis is continued until a pure green solution is obtained. The end-point of the reduction can be determined accurately by comparison with the color of a known vanadium (III) solution or by a control titration with $KMnO_4$. The reduced solution is allowed to stand in a closed vessel. Crystallization of the alum is complete within 2–3 days; the yield is 30–50%.

The H_2SO_4 quantity *a* used initially determines whether the red or the blue alum form will be obtained. When $a = 20$ g., pure red crystals result, whereas when $a = 40$ g., the crystals are pure blue.

PROPERTIES:

Red or blue crystals; effloresce slowly in air with loss of water and oxidation. At 40–50°C, the alum melts in its water of crystallization, affording a green mass. Solubility (20°C): 40 g./100 g. H_2O. d 1.687.

K, Rb AND Cs VANADIUM (III) ALUMS

The preparation of these compounds is similar to that of the NH_4 alum. The starting material is either V_2O_5, which is converted to a $VOSO_4$ solution by treatment with H_2SO_4 and SO_2, or a $VOSO_4$ compound. The stoichiometric quantity of K_2SO_4, Rb_2SO_4 or Cs_2SO_4 is added and the mixture is then electrolytically reduced. The ease and completeness of precipitation of these alums from their green solutions increase (and their solubility decreases) in the order K → Rb → Cs.

REFERENCES:

A. Piccini, Z. anorg. Chem. 11, 106 (1896); 13, 441 (1897); A. Billtemann, Z. Elektrochem. 10, 141 (1904); J. Meyer and E. Markowicz, Z. anorg. allg. Chem. 157, 211 (1926); H. Hartmann and H. L. Schäfer, Z. Naturforsch. 6a, 754 (1951).

Vanadium (IV) Oxysulfate

(Vanadyl Sulfate)

$VOSO_4$

$VOSO_4 \cdot 3H_2O$

A solution of V_2O_5 in pure sulfuric acid is reduced, preferably with SO_2 (which is easier to work with than oxalic acid and ethanol because its excess may be readily removed).

$$\underset{181.9}{V_2O_5} + \underset{98.1}{H_2SO_4} + \underset{21.9\ l.}{SO_2} + 5\,H_2O = 2\ \underset{434.1}{VOSO_4 \cdot 3H_2O}$$

DropBooks

Thus a stiff paste is prepared by stirring 190 g. of mildly calcined V_2O_5 with 110 ml. of conc. H_2SO_4 and 50 ml. of H_2O; considerable heat is evolved during this operation. On the next day, 100 ml. of H_2O is added and SO_2 introduced while heating the mixture on a water bath, until nearly all of the V_2O_5 is dissolved. The dark-blue filtered solution is concentrated on a slowly boiling water (or steam) bath until a thick crystal mass is formed; the crystals are then suction-filtered and washed acid-free with 96% ethanol. The undesirable formation of a thick, blue sirup or a hard crystal cake, mentioned in the literature, seems to be due to impurities or to reaction conditions which differ from those given here; no such inconveniences are encountered when V_2O_5, prepared from thrice-recrystallized NH_4VO_3, and SO_2 as the reducing agent are used according to the above procedure. The bright, light-blue crystalline powder is dried over P_2O_5 in a vacuum desiccator. Yield: 235 g. of $VOSO_4 \cdot 3\,H_2O$. Evaporation of the mother liquor affords another crop of less pure vanadyl sulfate.

PROPERTIES:

Sky-blue crystalline powder. Readily soluble in H_2O, sparingly in ethanol. Hygroscopic; indefinitely stable in a closed bottle provided oxygen is absent.

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L. Vanino. Handb. d. präp. Chemie, Anorg. Teil [Handbook of Preparative Chemistry, Inorg. Part], 3rd ed., Stuttgart, 1925, p. 677; J. Dehnert. Thesis, Univ. of Jena, 1952, and a personal communication.

$VOSO_4$, anhydrous

$$\underset{181.9}{V_2O_5} + 2\,\underset{196.2}{H_2SO_4} = 2\,\underset{326.0}{VOSO_4} + \underset{36.0}{2\,H_2O} + {}^1/_2\,O_2$$

Analytical grade conc. H_2SO_4 (100 ml.) and 3 g. of V_2O_5 are boiled for several hours in a long-neck, round-bottom flask. The product is cooled (first in air, then in ice), and poured into 500-700 ml. of H_2O. The solid is suction-filtered until dry and washed with a large quantity of water. Since the product is still heterogeneous (yellow-brown particles, in addition to green ones), it is again subjected to the same treatment and, after suction-filtration, dried with ethanol and ether, or over H_2SO_4 in a desiccator.

PROPERTIES:

Green, loose, granular to finely crystalline powder; virtually insoluble in H_2O.

REFERENCES:

A. Sieverts and E. L. Müller. Z. anorg. allg. Chem. 173, 313 (1928); V. Auger. Comptes Rendus Hebd. Séances Acad. Sci. 173, 306 (1921).

Vanadium Nitrides

VN

I. If pure V metal is available, it is best to proceed via the syntheses:

$$\underset{51.0}{V} + {}^1/_2\,\underset{11.2\ l.}{N_2} = \underset{65.0}{VN}; \qquad \underset{51.0}{V} + \underset{23.4\ l.}{NH_3} = \underset{65.0}{VN} + {}^3/_2\,H_2$$

which give the purest products. Depending on the metal particle size, a reaction temperature between 900 and 1300°C is required. The starting material is placed in a boat (or crucible) made of Al_2O_3 or Mo metal (see also the preparation of TiN, p. 1233, and of NbN, p. 1328). When other preparative methods are used, particularly those employing oxygenated starting materials (as in the

method described below), the nitride product inevitably contains some oxygen.

Alternate methods:

II. Very pure NH_4VO_3 is heated for several hours at 900–1000°C in a very dry NH_3 stream.

III. $VOCl_3$ or V_2O_3 is heated in an NH_3 stream.

IV. $V_2O_3 + 3\ C + N_2 = 2\ VN + 3\ CO$.

V. Deposition from gas phase on an incandescent wire; the gas contains VCl_4, H_2 and N_2. (see also TiN, p. 1233).

V_2N

I. Vanadium nitride, VN, is intimately mixed with the stoichiometric quantity of V metal powder; either the loose or the compacted mixture is then heated at 1100–1400°C in an Al_2O_3 or Mo crucible under Ar.

PROPERTIES:

Dark, submetallic materials.

VN: M.p. 2050°C; d 6.04. Homogeneity region: $VN_{1.00}$–$VN_{0.71}$. Crystal structure: B1(NaCl) type.

V_2N: Homogeneity region: $VN_{0.50}$–$VN_{0.37}$. Crystal structure: L 3 type.

DropBooks

REFERENCES:

I, II. H. Hahn. Z. anorg. Chem. 258, 58 (1949); V. E. Epelbaum and A. Brager. Acta Physicochim. URSS 13, 595 (1940); W. D. Schnell. Thesis, Univ. of Freiburg i. Br., 1960.

III. H. W. Roscoe. Ann. Pharm. Suppl. 6, 114(1868); 7, 191 (1870); N. W. Whitehouse. J. Soc. Chem. Ind. 27, 738 (1907).

IV. E. Friederich and L. Sittig. Z. anorg. allg. Chem. 143, 293 (1925).

V. A. E. van Arkel and J. H. de Boer. Z. anorg. allg. Chem. 148, 345 (1925); K. Moers. Z. anorg. allg. Chem. 198, 243 (1931).

Vanadium Phosphides

VP_3, VP, $VP_{<1}$

Vanadium phosphides are synthesized from the purest V metal available and P.

$$\underset{51.0}{V} + \underset{62.0}{2P} = \underset{113.0}{VP_2}; \qquad \underset{51.0}{V} + \underset{31.0}{P} = \underset{82.0}{VP}$$

Phosphorus and vanadium, the latter contained in an Al_2O_3 crucible, are placed in a quartz tube of the type used for the "Faraday synthesis" (see p. 76 f.). The tube is thoroughly evacuated, melt-sealed and then heated for 24–48 hours in such

way that the average temperature of the metal is 700–1000°C and that of the P is 480–550°C. To achieve homogeneous products and high P contents, the reaction must be carried out in stages, with intermediate grinding of the materials. Atmospheric oxygen must be carefully excluded during the grinding, to avoid appreciable absorption by the products.

The *V–P system* contains the phases VP_3 and VP, as well as several phases in which the P content is low.

In the preparation of VP_3, an excess of P must be used from the very start because VP, once formed, reacts extremely slowly with additional phosphorus.

The vanadium phosphide VP can be obtained not only via the above synthesis, but also by thermal degradation of VP_3 at 700–900°C (vacuum).

Lower phosphides (including V_3P) are obtained by synthesis from the elements or from VP and V.

Alternate method: Electrolysis of V_2O_5-containing phosphate melts, with cathodic reduction to vanadium phosphides [M. Chène, Comptes Rendus Hebd. Séances Acad. Sci. 208, 1144 (1939); Ann. chimie [11], 15, 272 (1941)].

PROPERTIES:

Dark-gray substances; the lower phosphides have a submetallic luster. Not attacked by dilute H_2SO_4. Attacked by conc. H_2SO_4 the more readily, the lower the phosphorus content. Incompletely soluble in nitric acid and aqua regia. Can be analyzed after decomposition by fusion with sodium carbonate–sodium nitrate.

VP: d 4.7; $VP_{0.35}$: d 5.4.

REFERENCE:

M. Zumbusch and W. Biltz, Z. anorg. allg. Chem. 249, 1 (1942).

Vanadium Carbides

VC, V_2C

I. It is probable that pure products can be obtained only by synthesis from the elements:

$$\underset{51.0}{V} + \underset{12.0}{C} = \underset{63.0}{VC}; \quad \underset{101.9}{2V} + \underset{12.0}{C} = \underset{113.9}{V_2C}$$

The reactants, preferably in finely subdivided form, are intimately mixed and, if needed, also compressed into pellets. The reaction is then carried out in a high vacuum. At a temperature of 1200°C, approximately 24 hours, or at 2000°C about 15 minutes, are required for homogenization of the product. The reaction is best carried out in a graphite crucible.

Alternate methods: a) The elements are combined by heating in a carbon arc [A. Morette and M. G. Urbain, Comptes Rendus Hebd. Séances Acad. Sci. 202, 572 (1936)].

b) Vanadium oxides are mixed with carbon and heated in a H_2 stream or in high vacuum. Carbides of an increased degree of purity are obtained if the final temperatures are allowed to reach 1700–2100°C (see the corresponding preparation of TiC, p. 1245 ff.) [C. Agte and K. Moers, Z. anorg. allg. Chem. 198, 233 (1931); E. Friederich and L. Sittig, Z. anorg. allg. Chem. 144, 169 (1925); A. Morette, Bull. Soc. Chim. France [5], 5, 1063 (1938); W. Dawihl and W. Rix, Z. anorg. Chem. 244, 191 (1940)].

c) Vapor deposition method (see TiC, p. 1246). An H_2 stream containing VCl_4 and toluene vapors is passed over an incandescent W wire [K. Moers, Z. anorg. allg. Chem. 198, 243 (1931)].

PROPERTIES:

Dark, very hard, chemically resistant submetallic substances. The V–C system has two phases:

VC: Homogeneity region $VC_{0.82}$–$VC_{0.74}$; m.p. 2800°C. Crystal structure: B 1 (NaCl) type.

V_2C: Homogeneity region $VC_{0.4}$–$VC_{0.5}$. Crystal structure: L 3 type.

DropBooks

REFERENCES:

A. Osawa and M. Oya. Sci. Rep. Tohoku Imp. Univ. 19, 95 (1930); Chem. Zentr. 1930, II, 298; W. Rostoker and A. Yamamoto. Trans. Amer. Soc. Metals 46, 1136 (1954); N. Schönberg. Acta Chem. Scand. 8, 624 (1954); M. A. Gurevich and B. F. Ormont. Zh. Neorg. Khimii 2, 1566 (1957); W. D. Schnell. Thesis, Univ. of Freiburg i. Br., 1960.

Dibenzenevanadium (0)

$$V(C_6H_6)_2$$

$$\underset{192.8}{VCl_4} + \underset{27.0}{Al} + 2\,\underset{156.2}{C_6H_6} \xrightarrow{AlCl_3} \underset{376.0}{V(C_6H_6)_2\,AlCl_4}$$

$$5\,V(C_6H_6)_2^{+} + 8\,OH^{-} = 4\,V(C_6H_6)_2 + VO_4^{3-} + 4\,H_2O + 2\,C_6H_6$$

The reactor is a 250-ml., three-neck flask equipped with an agitator, a reflux condenser and a mercury safety valve. A mixture

of 10 g. (0.37 moles) of dry Al powder and 4 g. (0.03 moles) of finely subdivided $AlCl_3$ and 150 ml. of absolute benzene (an excess) is added. The system is purged by introducing N_2 via the reflux condenser. The flask is equipped with a pressure-equalizing dropping funnel containing a solution of 9 g. (5 ml., 0.047 moles) of freshly distilled VCl_4 in 50 ml. of benzene. The flask contents are heated to a boil while stirring under a blanket of N_2. The VCl_4 solution is then added dropwise (slowly) over a period of one hour, and the mixture is agitated and boiled for an additional 20 hours. It assumes a golden yellow color. It is allowed to cool, and the dropping funnel, the agitator and the reflux condenser are replaced (under a N_2 stream) with stoppers and a vacuum adapter. The benzene is then removed in vacuum, with heating toward the end of the distillation. The dry residue is reduced to small pieces (in the same flask and under N_2). While protecting it from air, a part of the residue is then transferred to a 500-ml. separatory funnel kept under N_2 (which is introduced through a side tube), and covered with 200 ml. of N_2-saturated petroleum ether. This is followed by repeated additions, with vigorous shaking, of 100-ml. portions of N_2-saturated 1 N NaOH. After complete hydrolysis, the mixture is allowed to stand, the aqueous layer is separated, and the brown-red petroleum ether solution is washed three times (in the absence of air) with 20-ml. portions of N_2-saturated H_2O. Hydrolysis of the remainder of the solid reaction product is carried out similarly, in 2-3 operations. The combined petroleum ether extracts are dried for 15 minutes over solid KOH and the solvent is evaporated in vacuum. The residue is sublimed at 120-150°C in high vacuum, placed in a V-shaped washing tube, washed three times with 5-10 ml. of air-free, absolute petroleum ether to remove organic impurities, and finally resublimed. Yield: 1.3-2.5 g. (13-25%, based on VCl_4).

PROPERTIES:

Formula weight 207.18. Brown-red to black crystalline substance. M.p. (in N_2) 277°C. Sublimes in high vacuum at 120-150°C, decomposes above 300°C. Instantly oxidized by air (decomposition). Soluble in benzene, ether, pyridine, petroleum ether and acetone; the solutions are brown-red and stable in the absence of air. Insoluble or only sparingly soluble in CCl_4 and methanol. Not dissolved or attacked by H_2O in the absence of O_2, but decomposed in the presence of air.

REFERENCE:

E. O. Fischer and H. P. Kögler, Chem. Ber. 90, 250 (1957).

Potassium Hexathiocyanatovanadate (III)

$K_3V(SCN)_6$

A vanadium (III) solution is obtained from V_2O_5 by reduction of the latter with SO_2, followed by electrolysis. This solution is then reacted with KSCN:

$$\underset{181.9}{V_2O_5} + 5\,H_2SO_4 + \underset{1166.2}{12\,KSCN} + 4\,e^- = \underset{1033.5}{2\,K_3V(SCN)_6} + \underset{522.8}{3\,K_2SO_4} + \underset{90.1}{5\,H_2O} + 2\,SO_4^{--}$$

Fine V_2O_5 powder (91 g., 0.5 moles) is stirred with 250 ml. of 4 N H_2SO_4, the suspension heated, and SO_2 introduced until a clear, pure blue solution is obtained. The mixture is heated to a boil to remove the excess SO_2 and is then concentrated to 2/3 of its previous volume.

This solution is subjected to electrolytic reduction in a cell containing a clay cylinder diaphragm; the current is 2–3 amp. at 10 v. (the procedures are those described on pp. 1277 and 1284). The electrolysis is continued until the electrolyte at the cathode shows the pure green color of vanadium (III). The best electrodes are those made of platinum sheet.

The theoretical quantity of KSCN used depends on the volume of the cathode electrolyte and is calculated on the assumption that 6 moles (or 583 g. of KSCN) corresponds to 1 g.-atom of vanadium. This quantity of KSCN, in the form of a concentrated aqueous solution, is then added to the above electrolyte. The resulting red liquid is concentrated on a water bath; the residue is dissolved in the minimum amount of ethanol and treated with ether until K_2SO_4 no longer precipitates. The K_2SO_4 is filtered off, the filtrate is evaporated on a water bath, and the precipitation operation is repeated. The residue thus obtained (it is completely free of K_2SO_4) is recrystallized from a small amount of H_2O. Well-formed crystals of the dihydrate, $K_3V(SCN)_6 \cdot 2\,H_2O$, are obtained.

The anhydrous salt is obtained by drying the dihydrate over H_2SO_4 in a vacuum desiccator, finely pulverizing it, and then completely dehydrating it under vacuum (drying pistol) at 95°C until constant weight is reached.

PROPERTIES:

$K_3V(SCN)_6 \cdot 2\,H_2O$: Formula weight 552.79. Brown-red, leaf-like crystals.

$K_3V(SCN)_6$: Formula weight 516.76. Very hygroscopic.

REFERENCE:

O. Schmitz-Dumont and G. Broja. Z. anorg. Chem. 255, 299 (1948).

ProfBooks

Niobium Metal, Tantalum Metal

Because of the tendency of Nb and Ta metal to form very stable oxides, nitrides and carbides, the difficulties in the preparation of these metals are similar to those encountered in the preparation of Ti and Zr (see pp. 1161 and 1172).

Three methods are available for industrial preparation of the pure metals. The first involves electrolysis of fluoride melts containing K_2NbOF_5 (or K_2TaF_7), as well as a certain amount of the corresponding oxides, Nb_2O_5 or Ta_2O_5. An iron fusion pot serves as the cathode and graphite rods as the anodes. The resulting metal is a fine powder which may be separated from the admixed salt melt by a variety of processes. In the second method an oxide and a carbide, for instance $Nb_2O_5 + 5\ NbC$, are mixed, compressed into pellets and heated in high vacuum to temperatures exceeding 1600°C. In the third method, a double fluoride is reduced either with liquid sodium or sodium vapor. In each case, the material is processed further via powder-metallurgical methods, by subjecting it to repeated and alternating procedures which increase density and hot degassing treatments.

I. REDUCTION WITH SODIUM OR CALCIUM

The laboratory preparation of the metal powder proceeds via reduction of the halides with sodium, calcium or CaH_2.

Thus, for example, 50 g. of high-purity, dry K_2TaF_7 and 18 g. of Na (precut into small pieces under benzene) are placed in a heavy-wall steel vessel, tightly closed off with a well-fitting conical lid, which is fastened on with screws. The system is heated for one hour at red heat, allowed to cool completely, and reopened; the reaction mixture, which still contains some free Na, is carefully introduced, in small portions and with agitation, into 500 ml. of H_2O. The lumps disintegrate, and the resulting metal powder is treated several times with H_2O, then hot nitric acid (d 1.2), strong hydrochloric acid (1:1) and, finally, again and thoroughly with water. It is then dried.

According to Kroll, the oxides can be reduced with calcium metal in the presence of $CaCl_2$ as the fluxing agent

$$\underset{265.8}{Nb_2O_5} + \underset{200.4}{5\,Ca} = \underset{185.8}{2\,Nb} + \underset{280.4}{5\,CaO}$$

$$\underset{441.9}{Ta_2O_5} + \underset{200.4}{5\,Ca} = \underset{361.9}{2\,Ta} + \underset{280.4}{5\,CaO}$$

Redistilled Ca turnings of the best grade are used in approximately 30% excess. The presence of $CaCl_2$ is essential. For example, in a preparation of a small amount of metal, 8 g. of Nb_2O_5 (or 13 g. of Ta_2O_5), 8 g. of Ca and 15 g. of $CaCl_2$ are placed in a heavy-wall tubular iron crucible (25 mm. in diameter,

80 mm. long) which is filled with Ar and made gas-tight by closing it off with a welded-on (oxygen-acetylene flame) iron plug. This crucible is then heated for half and hour at about 1000-1100°C, allowed to cool completely, and sawed open. The contents are treated with water and acids, as described above. The metal powder contains some very fine particles which are best separated by decantation and discarded.

The above two methods are equally applicable to Nb and to Ta. Various modifications of these methods are possible; in particular, the reduction with Ca may be replaced by one with CaH_2 [see the corresponding procedures for Ti, methods I and II, pp. 1161-1165, as well as G. Tourné, Ann. Chim. [13], 4, 949 (1959)].

The metal powders thus obtained are not particularly pure and often contain not more than 97% of the metal, which is accompanied by hydrogen, some oxygen, and sometimes also small amounts of nitrogen, carbon and iron. The purity can be increased by repeating the treatment with the reducing metal or with CaH_2 and, also, by increasing the batch size. At any rate, it is of advantage to purify these powders further by heating them at a high temperature under vacuum, for example, via procedure II. However, the further conversion of Nb or Ta powder to the corresponding halides is not affected by the impurities, provided they are not metallic.

DropBooks

II. PURIFICATION BY CALCINATION

Low-purity Nb or Ta can be freed of most of its contaminants by heating to red heat in a vacuum. Both Nb and Ta have very high melting points, and thus the contaminants can simply be evaporated. In this procedure, the metal powder, pressed into oblong rods and clamped between water-cooled molybdenum jaws, is resistance-heated with a high current, or the loose or compressed metal powder is heated to red heat on a support of ThO_2, W or Ta sheet, placed in a tungsten electrical heating element. The best type of heater is the furnance shown in Part I, p. 40 f., wherein a tungsten tube or a tungsten trough is used as the heat conductor. High-frequency induction heating can also be used. In each case, a very high vacuum of at least 10^{-5} mm. is of controlling importance, if the purification is to be efficient. The material is first de-gassed by preheating it for about 1 hour at 1200°C. The tempera-ture is then slowly increased and then maintained at 2000-2200°C for some time (one to several hours). If this temperature is reached too quickly or if the vacuum is not good, no purification will be achieved; in addition, in the case of Nb, there will also be un-desirable melting, among other things (formation of a eutectic between metal and impurities).

III. CRYSTAL-GROWING (OR VAPOR-DEPOSITION) PROCESS

High-purity Nb or Ta can be obtained by deposition on an incandescent wire from gaseous $NbCl_5$ and $TaCl_5$, either in the presence or the absence of hydrogen. This crystal-growing process corresponds closely to that described for titanium on p. 1168 ff., particularly as far as the apparatus is concerned. Since tungsten and Nb or Ta readily form brittle alloys, a tungsten nucleating (substratum) wire cannot be used in this case; instead, one uses an approximately 0.1-mm. ϕ wire of the metal to be deposited. In addition, Ni (and not W) terminals are used, and the system is degassed by heating to red heat in vacuum before the start of the run. The chloride ($NbCl_5$ or $TaCl_5$) is introduced into the side tube and vacuum-sublimed in situ; the entire reactor system is heated and thoroughly degassed prior to sublimation, because the absence of gas is essential to the quality of the deposited metals. The reactor remains connected to the vacuum pump throughout the entire process. Vapor deposition takes place by heating the chloride and the entire vessel to about 100°C; the substratum wire is heated to 1800°C in the case of Nb, and to 2000°C in the case of Ta. The deposited metals are of very high purity.

The thickness of the incandescent wire changes continuously during the reaction, so that careful supervision of the process and good electrical control are imperative. This disadvantage is circumvented in Rolsten's modification of the process, whereby the volatile iodide of the metal is decomposed at 750-1100°C in an indirectly heated fused quartz (or Vycor) tube.

Alternate methods: a) Reaction of the chlorides with Mg [J. Prieto, A. J. Shaler and J. Wulff, Metals Technol. 14, No. 6 (1947)].

b) Reduction of the oxides with Si while volatilizing the nascent SiO [E. Zintl et al., Z. anorg. allg. Chem. 245, 1 (1940)].

IV. COMMINUTION OF THE SOLID METAL

Commercially available solid Nb and Ta (sheet, wire, etc.) are usually far purer than the powdered material. When metal powder of very highest purity is required for the preparation of a Nb or Ta compound, solid waste pieces may be used to advantage. They are pulverized by hydrogenation at 500-600°C (see hydrides) and cooling under H_2. The resulting hydrides are very brittle and are readily pulverized to the desired size. The powder thus obtained is then dehydrogenated at 1000°C in an extremely high vacuum. The decrease in purity occurring during these operations is negligibly small provided very pure H_2 is used, the pulverization of the hydrides is carried out in an inert gas atmosphere, and the

heating and degassing of the material is always carried out so slowly that no appreciably loss of vacuum occurs in the system (which is permanently connected to a vacuum pump).

PROPERTIES:

Nb: Atomic weight 92.91. M.p. 2468°C; d 8.58.
Te: Atomic weight 180.95. M.p. 3030°C; d 16.6.
These two metals are not attacked by mineral acids (with the exception of hydrofluoric); they are readily soluble in a mixture of concentrated hydrofluoric and nitric acids. Crystal structure: A 2 (W) type.

REFERENCES:

General: A. E. van Arkel. Reine Metalle [Pure Metals], Berlin, 1939; H. Funk. Die Darstellung der Metalle in Laboratorium [Laboratory Preparation of Metals], Stuttgart, 1938; Ullmans Enzyklopädie d. tech. Chemie [Ullman's Encyclopedia of Industrial Chemistry], 12, Munich-Berlin, 1960, Niobium, p. 736 ff.; G. L. Miller. Tantalum and Niobium, London, 1959.

I. K. R. Krishnaswami. J. Chem. Soc. (London) 1930, 1277; W. Kroll. Z. anorg. allg. Chem. 234, 42 (1937); J. W. Marden and M. N. Rich. U. S. Patent 1,728,941 (1927/29); G. Brauer. Unpublished experiments, Darmstadt, 1942; W. E. Dennis and A. F. Adamson. U.K.A.E.A. Techn. Note No. 92 (1954); E. F. Block. U.S. Bureau of Mines, paper given at the Achema meeting, Frankfurt, 1958.

II. H. Bückle. Z. Metallkunde 37 (Metallforschg. 1), 53 (1946); R. H. Myers. Metallurgia (Manchester) 38, 307 (1948); Symposium on the Metallurgy of Niobium, J. Inst. Metals 86 (1956-57); B. W. Gonser and E. M. Sherwood. The Technology of Columbium, New York-London, 1958.

III. W. G. Burgers and J. C. M. Basart. Z. anorg. allg. Chem. 216, 223 (1934); see also the literature cited in section on Ti, method V; R. F. Roisten. Trans. A.I.M.E. 215, 472 (1959); J. Electrochem. Soc. 106, 975 (1959); Z. anorg. allg. Chem. 305, 25 (1960).

Preprocks

Vanadium, Niobium and Tantalum Hydrides

After thorough degassing at red heat in vacuum, the metals are heated in an atmosphere of extremely pure H_2. The rate of hydrogen absorption depends strongly on the particle size of the metals, the metal purity and the pretreatment method. Above 400°C, even solid Nb and Ta (sheet, wire, etc.) react fairly rapidly. The rate of the reaction increases with the metal purity and is particularly

high if the metal history includes a previous hydrogenation and dehydrogenation. In that case, hydrogen is sometimes absorbed even at room temperature. Both the NbH and the TaH systems may exist in two stable phases; the transitions from one to another, however, are not clearly reflected in the isotherms and isobars of the H_2 equilibrium pressure. Hence, depending on the temperature and equilibrium H_2 pressure, the hydrogenated material may contain hydrogen in all ratios up to the limiting composition, which is approximately $NbH_{0.93}$ and $TaH_{0.8}$ (corresponding to 112 ml. of H_2/g. of Nb and 56 ml. of H_2/g. of Ta. One gram of V absorbs a maximum of 205 ml. of H_2, corresponding to the limiting formula $VH_{0.94}$.

The deuterides of Nb and Ta are analogous to the hydrides prepared under the same conditions.

PROPERTIES:

Lustrous metallic or metallic gray appearance, much like that of the free metals. The lower hydrides (up to approximately $MH_{0.1}$) are quite hard but are still ductile, increasing in brittleness with increasing H content and becoming extremely brittle at high hydrogen ratios. The hydrogen can be removed in a high vacuum at temperatures exceeding 400°C, and rapidly between 800 and 1000°C.

REFERENCES:

General: D. P. Smith, Hydrogen in Metals, Chicago, 1948.

V-H: L. Kirschfeld and A. Sieverts, Z. Elektrochem. 36, 123 (1930); H. Huber, L. Kirschfeld and A. Sieverts, Ber. dtsch. chem. Ges. 59, 2891 (1926); M. J. Trzeciak, D. F. Dilthey and M. W. Mallett, Batelle Mem. Inst. Rep. 1112 (1956).

Nb-H: A. Sieverts and H. Moritz, Z. anorg. allg. Chem. 247, 124 (1941); W. M. Albrecht, M. W. Mallett and W. D. Goode, J. Electrochem. Soc. 105, 219 (1958); 106, 981 (1959); S. Komjathy, J. Less Common Metals 2, 466 (1960).

Ta-H: A. Sieverts and H. Brüning, Z. phys. Chem. (A) 174, 365 (1935); A. Sieverts and E. Bergner, Ber. dtsch. chem. Ges. 44, 2394 (1911).

Niobium [II] Chloride

$NbCl_2$

$$\underset{92.9}{Nb} + \underset{398.6}{2\,NbCl_3} = \underset{491.5}{3\,NbCl_2}$$

Stoichiometric quantities of Nb metal powder and $NbCl_3$ are weighed under anhydrous conditions, triturated and placed in a quartz tube which is closed at one end. Constrictions *b* and *d* (Fig. 305) are then made in the end of the tube and it is connected to a high-vacuum source. (It should be remembered in calculating

the amount of $NbCl_3$ that this compound exhibits a considerable phase width and can, therefore, be of varying composition. The use of $NbCl_{2.67}$ is particularly convenient.)

To degas the contents, the reactor is heated for 12 hours in high vacuum at 200°C and is then melt-sealed at constriction *d*. The reaction is completed by heating the entire tube at 800°C for two to three days. The tube is then chilled in water and the fairly volatile by-products ($NbCl_5$, $NbOCl_3$) are distilled forward into tube section *c* by establishing a 200/20°C temperature gradient. The $NbCl_2$ remains in *a*.

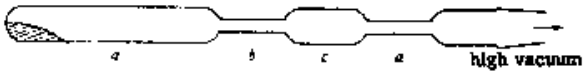

Fig. 305. Preparation of niobium (II) chloride. The quartz reactor is 8 mm. I.D. Length: *a* = 50 mm., *c* = 20 mm.

PROPERTIES:

Formula weight 163.82. Black-brown crystals. Stable in air, insoluble in H_2O and organic solvents. When heated in an evacuated tube, the $NbCl_2$ decomposes at a temperature gradient of 800/550°C via the equilibrium reaction: $4\ NbCl_2 = Nb + 3\ NbCl_{2.67}$; at a temperature gradient greater than 800/20°C, the reaction is: $2\ NbCl_2 = Nb + NbCl_4$. Heating in air produces $NbOCl_3$ and Nb_2O_5.

Preparations

REFERENCES:

H. Schäfer and K. D. Dohmann. Z. anorg. allg. Chem. 300, 1 (1959); H. Schäfer and F. Kahlenberg. Z. anorg. allg. Chem. 305, 291 (1960).

Niobium (III) Chloride

$NbCl_3$

I. $$\underset{270.2}{NbCl_5} + \underset{22.4\ l.}{H_2} = \underset{199.3}{NbCl_3} + \underset{72.9}{2\,HCl}$$

High purity, oxygen-free hydrogen is passed through a vessel containing $NbCl_5$ heated to 150-190°C. The gas stream then passes through a Pyrex or Vycor tube heated to 400-530°C and solid precipitate of green-black $NbCl_3$ deposits on the walls. Complete conversion of $NbCl_5$ to $NbCl_3$ may be achieved, provided the gas rate is low. The lower partial pressures of $NbCl_5$ (at a saturation temperature of 150°C) and the higher temperature of the reaction zone (that is, 530°C) lead to a limiting composition, which is low in chlorine ($NbCl_{2.67}$).

Brubaker and Young prepared $NbCl_5$ from Nb metal and Cl_2 in the apparatus shown in Fig. 310; they then allowed it to sublime in an H_2 stream through constriction *c* into the right-hand tube, which was heated to 500°C and equipped with a cold finger. The $NbCl_3$ separated both as a dark crust on the tube wall and as a cone-shaped deposit on the cold finger. The product may be pyrophoric when prepared by this procedure; it should, therefore, be handled only under a protective N_2 blanket.

II. $$\underset{810.6}{3\,NbCl_5} + \underset{185.8}{2\,Nb} = \underset{996.4}{5\,NbCl_3}$$

High-surface Nb metal (e.g., foil) and a slight excess of $NbCl_5$ are placed in an evacuated reactor tube which is then sealed. (The $NbCl_5$ can be prepared in the reactor itself before introducing the Nb metal; this can be accomplished by reacting weighed amounts of Nb_2O_5 and CCl_4—see preparation of $NbCl_5$, method III.) The sealed horizontal reactor is heated for three days in a temperature gradient such that the end of the tube containing Nb is at 390°C, while the remainder of the tube is at 355°C. The contents are thus converted to $NbCl_3$, which, as a result of the reversible equilibrium $NbCl_3$ (solid) + $NbCl_5$ (gas) = $2NbCl_4$ (gas), is transported into the 355°C zone where it deposits as crystals. It can then be resublimed by reversing the temperature gradient. At the end of the procedure, only the part of the tube containing the $NbCl_3$ is heated for a few minutes to 390°C while keeping the other end at 20°C, thus driving the $NbCl_5$ to the cold end. The tube is allowed to cool and is then opened under anhydrous conditions.

The partial pressure of $NbCl_5$ and, hence, the composition of the $NbCl_3$ phase can be varied in this synthesis by varying the ratio of the $NbCl_5$ to the volume of the sealed tube (saturation pressure of $NbCl_5$ at 355°C is 8 atm.).

III. $$\underset{810.6}{3\,NbCl_5} + \underset{53.9}{2\,Al} = \underset{597.8}{3\,NbCl_3} + \underset{266.7}{2\,AlCl_3}$$

Sublimed $NbCl_5$ is heated with a less than stoichiometric quantity of Al powder in an evacuated, sealed tubular reactor. For example, 1.2 g. of $NbCl_5$ and 0.08 g. of Al may be used. The entire length of the tube is heated to 275°C for about 40 hours. It is then placed in a temperature gradient, with the main section encased in an aluminum block at 300°C and the protruding end at room temperature. The partially formed $NbCl_4$ decomposes into $NbCl_3$ and $NbCl_5$, the excess $NbCl_5$ and $AlCl_3$ sublime into the tube end, while the green-black $NbCl_3$ remains in the main (lower) section of the tube. It is recovered by opening the tube; no special precautions against air are needed. The product of this process usually contains a small amount of Al_2O_3 (about 0.7%) which is introduced with the Al powder.

Alternate methods: a) Reduction of $NbCl_5$ with activated (excitation) H_2 at 200°C [V. Gutmann and H. Tannenberger, Monatsh. Chem. 87, 769 (1956)].

b) Preparation from Nb metal in an HCl stream at 300°C. A mixture of $NbCl_3$ and $NbCl_5$ is obtained [V. Y. Spitsyn and N. A. Preobrazhenskiy, Zh. Obshch. Khimii 10, 785 (1940); C. H. Brubaker and R. C. Young (1951)].

PROPERTIES:

Green-black; crystallizes in crusts, rods, or plates. Under sufficiently high $NbCl_5$ pressure and in the absence of air, $NbCl_3$ is stable at 800°C. It disproportionates to $NbCl_5$ and Nb in a temperature gradient. Only slightly air-sensitive at room temperature. Insoluble in H_2O, dilute acids and dilute alkali. Attacked by oxidizing agents at varying rates depending on the concentration and the temperature. Insoluble in organic solvents, even in ethanol.

Exhibits a rather wide homogeneity region (between $NbCl_{3.18}$ and $NbCl_{2.87}$). d 3.75.

REFERENCES:

I. P. Süe. Bull. Soc. Chim. France [5] 6, 830 (1939); H. Schäfer and C. Pietruck. Z. anorg. allg. Chem. 266, 151 (1951); C. H. Brubaker and R. C. Young. J. Amer. Chem. Soc. 73, 4179 (1951); H. Schäfer and K. D. Dohmann (1959).
II. H. Schäfer and K. D. Dohmann. Z. anorg. allg. Chem. 300, 1 (1959).
III. H. Schäfer, G. Göser and L. Bayer. Z. anorg. allg. Chem. 265, 258 (1951).

PrepBooks

Niobium (IV) Chloride

$NbCl_4$

Prepared by reduction of $NbCl_5$.

I. $$\underset{540.4}{2\,NbCl_5} + \underset{55.9}{Fe} = \underset{469.5}{2\,NbCl_4} + \underset{126.8}{FeCl_2}$$

The reaction is carried out in a sealed tube divided into two sections by a constriction, as shown in Fig. 306. The $NbCl_5$ (3 g.) is introduced into the closed tube end *a* by connecting the tube via its still open end *b* to the apparatus used for isolation of $NbCl_5$ (Fig. 309). Pure iron (0.24 g., e.g., Armco iron turnings or reduced iron) is placed in section *b*, the tube is drawn out to a

point, high vacuum is applied, and the tube is sealed at the point. The horizontal sealed tube is encased in two closely spaced aluminum blocks which are electrically heated to two different temperatures. The section containing $NbCl_5$ is heated to 195°C, and that with Fe to 400°C. The reaction time is at least 40 hours. The gaseous $NbCl_5$ is reduced and $NbCl_4$ separates as well-formed crystals in a transition region between the two temperature zones. The $FeCl_2$ (which at 400°C is still not very volatile) and unreacted $NbCl_5$ are found in the other sections of the tube.

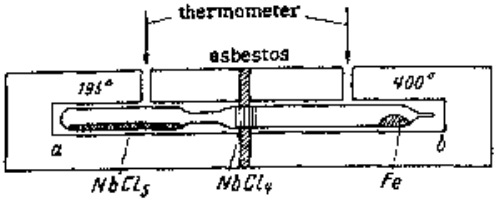

Fig. 306. Preparation of niobium (IV) chloride.

To prevent scattering of the reaction products by a rapid influx of gas (dry air, CO_2 or N_2) while opening the evacuated tube, the tip of the tube should be scratched, placed in a slightly larger vacuum hose, and broken off under vacuum. The tube may then be gradually filled with gas through the vacuum hose. To isolate the $NbCl_4$, the tube is then broken at an appropriate spot.

II. The $NbCl_5$ can also be reduced with Nb metal.

$$\underset{1080.8}{4\,NbCl_5} + \underset{92.9}{Nb} = \underset{1173.7}{5\,NbCl_4}$$

Thus, $NbCl_5$ and an excess of Nb metal are sealed into a tube described in method I and heated in the same temperature gradient; the reaction is complete in about 16 hours.

Alternate methods: a) Reduction of $NbCl_5$ with Al metal; requires a subsequent distillation of excess $NbCl_5$ and $AlCl_3$.

b) Reduction of $NbCl_5$ with H_2 at 2 atm. (generated when the tube is filled at STP, sealed and then heated). The reaction does not go to completion and $NbCl_5$ and $NbCl_4$ must be separated by sublimation.

c) Reaction of $NbCl_5$ and $NbCl_3$; as in most methods, an excess of $NbCl_5$ is usually required to depress the decomposition of $NbCl_4$.

PROPERTIES:

Brown-black crystal needles; pure brown in transmitted light. Sublimable at about 275°C, provided decomposition into $NbCl_5$ and

$NbCl_3$ is prevented by a sufficiently high $NbCl_5$ pressure. Decomposes on exposure to air and moisture (color change first to black, then to white). Dissolves in a small amount of H_2O and in dilute hydrochloric acid, giving a dark-blue solution.

REFERENCES:

H. Schäfer, C. Göser and L. Bayer. Z. anorg. allg. Chem. 265, 258 (1951); data from the Chemical Laboratory of the University, Freiburg i. Br., 1952; H. Schäfer, L. Bayer and H. Lehmann. Z. anorg. allg. Chem. 268, 268 (1952).

Tantalum (IV) Chloride

$TaCl_4$

I. $$\underset{1433.0}{4\,TaCl_5} + \underset{181.0}{Ta} = \underset{1614.0}{5\,TaCl_4}$$

A quartz reactor tube with a narrow hooked constriction, shown in Fig. 307 (I), is thoroughly degassed by heating in a high vacuum; then, 4 g. of Ta metal (preferably foil) and 10–15 g. of $TaCl_5$ are introduced into the tube on opposite sides of the constriction, and the tube is sealed under high vacuum. It is then heated in a slanted position in a temperature gradient so that the liquid $TaCl_5$ (in the higher end of the tube) is at 280°C and the Ta at 630°C. The nascent

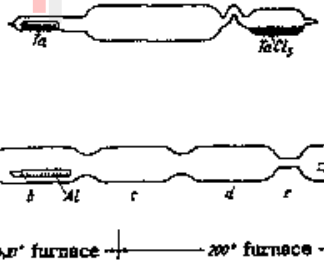

Fig. 307. Preparation of tantalum (IV) chloride. *b*) aluminum foil; *f*) $TaCl_5$.

$TaCl_4$ deposits in the 280° zone (large crystals) but is separate from the $TaCl_5$. A six-day run yields 8–10 g.; there is also a residue of unreacted starting materials. Before opening the tube, the reactor is cooled, and the section containing $TaCl_4$ is reheated to 200°C to separate any admixed $TaCl_5$ by sublimation. The opening of the tube and handling of $TaCl_4$ should be carried out in the absence of moisture.

II. $$\underset{1074.7}{3\,TaCl_5} + \underset{27.0}{Al} = \underset{968.3}{3\,TaCl_4} + \underset{133.4}{AlCl_3}$$

The reaction is carried out in a sealed reactor tube (Fig. 307, II) in a high vacuum. Aluminum foil (for example, 50 mg.) is introduced at *b*, while $TaCl_5$ (4–5 g.) in an ampoule is at *f*; both are introduced under anhydrous conditions. The $TaCl_5$ is made to sublime (in high vacuum) toward tube section *d*, and the tube is sealed off at constrictions *a* and *e*. The sealed tube is heated for 70 hours in a temperature gradient (see Fig. 306) such that *b* is at 400°C and the remainder of the tube at 200°C. The $TaCl_4$ deposits at *c* as large crystals. The tube is allowed to cool and only section *c* is reheated to 200°C to remove any $TaCl_5$ present in it.

III. $$\underset{358.2}{TaCl_5} + H = \underset{322.8}{TaCl_4} + HCl$$

Whereas $TaCl_5$ reacts with molecular H_2 only at temperatures exceeding 500°C (to form Ta metal), the reduction of $TaCl_4$ with H_2 activated by a high-frequency electrical discharge can be carried out at 200°C. The apparatus is the same as that for the preparation of $TaBr_4$ (Fig. 311) and the process is the same in all its details. A two-hour run completely reduces 1 g. of $TaCl_5$.

PROPERTIES:

Brown-black crystals. Moisture-sensitive; decomposes with oxidation on exposure to air. On heating in vacuum, disproportionates to $TaCl_5$ and a lower chloride; on heating in air forms Ta_2O_5 and volatile $TaCl_5$. Partly soluble in H_2O and dilute acids, yielding coffee-brown solutions; an insoluble dark material is also formed.

REFERENCES:

I. H. Schäfer and F. Kahlenberg. Z. anorg. allg. Chem. 305, 178 (1960).
II. H. Schäfer and L. Grau. Z. anorg. allg. Chem. 275, 198 (1954).
III. V. Gutmann and H. Tannenberger. Monatsh. Chem. 87, 769 (1957).

Niobium (V) and Tantalum (V) Chlorides

$NbCl_5$, $TaCl_5$

$NbCl_5$

I. $$\underset{92.9}{Nb} + \underset{56\,l.}{5/2\,Cl_2} = \underset{270.2}{NbCl_5}$$

Niobium metal, either as a powder or as a solid, can be readily chlorinated in a Cl_2 stream. The reaction is best carried out in a

tube similar to that shown in Fig. 312 (preparation of $NbBr_5$); however, the saturation tube is replaced by a T connector through which the sealed tube can be evacuated or dry N_2 or Cl_2 introduced. The end arrangement of the apparatus varies depending on the expected amount of $NbCl_5$. Air must be carefully displaced by evacuation or purging with N_2. The reaction with Cl_2 starts at 125–240°C; at 240°C, it takes only a few fours regardless of the Nb particle size. The absorption of Cl_2 is usually quite rapid. The $NbCl_5$ product is taken out under anhydrous conditions and resublimed in an appropriate manner (the apparatus of Fig. 308 can be used).

II.
$$\underset{265.8}{Nb_2O_5} + 5\,\underset{594.9}{SOCl_2} = 2\,\underset{540.4}{NbCl_5} + 5\,\underset{320.3}{SO_2}$$

A common, carefully dried bomb tube is charged with 2.7 g. of Nb_2O_5 and 10 ml. of $SOCl_2$. Care should be taken in the preparation of Nb_2O_5 (from precipitated hydrated oxide) not to exceed 400°C, since excessively calcined oxide is inactive and reacts incompletely. Thus, if the oxide is excessively calcined, it is fused with $KHSO_4$, the melt hydrolyzed, the hydrated oxide precipitated with ammonia and then dried for a long time at about 400°C. Before use, the $SOCl_2$ is purified by first refluxing it for 4 hours in the presence of S and then fractionally distilling it in a column [D. L. Cottlet, J. Amer. Chem. Soc. 68, 1380 (1946)].

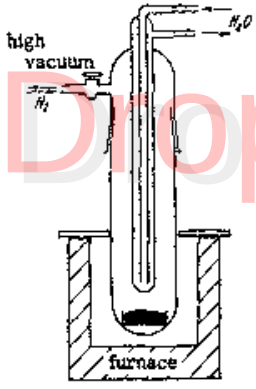

Fig. 308. Resublimation of niobium and tantalum pentahalides under anhydrous conditions.

The filled and sealed tube is heated for 3 hours at 200°C. On slow cooling, $NbCl_5$ crystallizes in needles. The tube is cooled to −10°C, opened, and the SO_2 discharged by heating to room temperature; the excess $SOCl_2$ is removed by further slight heating in vacuum. To achieve this, as well as for the further handling of $NbCl_5$, the apparatus shown in Fig. 309 is attached to the open bomb. Because of the high sensitivity to moisture exhibited by $NbCl_5$, it is absolutely necessary to equip the apparatus with devices which permit handling of the product in such a way that even traces of moisture will be excluded. The $NbCl_5$ remaining at *a* is first moved to *b* by subliming it under vacuum; it is then transferred to *g* (under nitrogen) for further handling. This is achieved by removing the ground cap *c*, stretching a thin perforated rubber

cap over the tube and introducing through this cap a small spatula with a long handle. Tube *g* of Fig. 309 is used for storing the product; it is closed at *f* with a ground glass stopper and permits partial removal of the chloride. Protection from moisture is provided by N_2, which is introduced through *h*. Naturally, other types of containers can be used instead of *g*, for example, a simple ampoule which is sealed off.

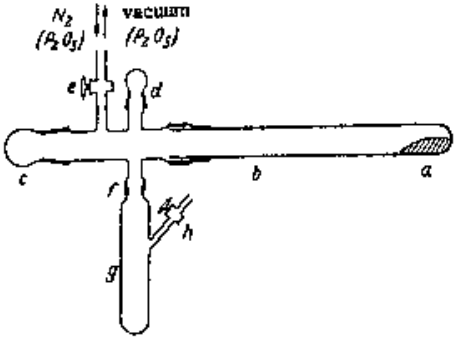

Fig. 309. Purification by sublimation and filling of a vessel with niobium (V) chloride. *a*, *b*) bomb tube; *c*, *d*) openings for introducing spatulas and long-handle hooks; *g*) storage vessel.

III. The oxide can also be chlorinated with CCl_4 in a similar fashion:

$$\underset{265.8}{Nb_2O_5} + \underset{1269.2}{5\,CCl_4} = \underset{540.4}{2\,NbCl_5} + \underset{494.6}{5\,COCl_2}$$

In this method (which was originally developed for analytical purposes) 1 g. of oxide and 4 ml. of CCl_4 are heated for 5-10 hours at 270-300°C in a sealed tube. It is not absolutely necessary to remove the air from the tube before the reaction. After opening the tube, which should be done with the usual precautions, the reactants are distilled off. The $NbCl_5$ is resublimed under vacuum and isolated as described in method II. Because of the high pressures developed in the sealed tube, this method is limited to small quantities of reactants [E. R. Epperson et al., Inorg. Syntheses 7, 163 (1963)].

Alternate methods:

IV. $$Nb_2O_5 + 5\,C + 10\,Cl_2 = 2\,NbCl_5 + 5\,COCl_2$$

In this very old method, the oxide is mixed with purified sugar charcoal in a 1:4 molar ratio. The granular mixture is placed (without a boat) in a tube of high-melting (Pyrex or Vycor) glass.

Beyond the mixture (in the direction of gas flow) there is a fairly long bed of pure charcoal. Before starting the chlorination, both layers are dehydrated by heating to 500°C in a stream of very pure N_2. Very pure, O_2-free Cl_2 is then passed through while heating the mixture to 280–350°C and the adjacent charcoal layer to 750°C. The $NbCl_5$ receiver is sealed directly onto the reactor via a constriction. During the reaction (3 hours for 8 g. of Nb_2O_5 and 32 g. of C) the constriction must be checked to make sure that it does not become plugged with $NbCl_5$. The formation of the by-product $NbOCl_3$, which is usually difficult to avoid in this reaction, is almost completely prevented under these conditions. In spite of this, separation of the $NbCl_5$ from the $NbOCl_3$ by careful fractional sublimation is recommended. [P. Süe, Bull. Soc. Chim. France [5] 6, 830 (1939); R. F. Rolsten, J. Amer. Chem. Soc. 80, 2952 (1958)].

V.

$$Nb_2O_5 + 5\,CCl_4 \xrightarrow{(Cl_2)} 2\,NbCl_5 + 5\,COCl_2$$

A chlorine stream containing CCl_4 vapor (the stream is saturated by bubbling through a CCl_4-containing wash bottle) is reacted with the oxide held in a boat which is inserted into a tube of high-melting glass or, better, a quartz tube. The reaction temperature is 300–400°C. Quite often, $NbOCl_3$ is also formed as a by-product [Gmelin-Kraut, Handbuch anorg. Chem. [Handbook of Inorganic Chemistry], 7th ed., Vol. IV/1, Heidelberg, 1928, p. 236].

VI. $NbS_2 + 3/2\,Cl_2 = NbCl_5 + S_2Cl_2$

[O. Hönigschmid and K. Wintersberger, Z. anorg. allg. Chem. 219, 161 (1934).]

PROPERTIES:

Yellow, granular to needle-shaped crystals; dark-red when contaminated with 1 mole % of WCl_6. M.p. 204.5°C, b.p. 254°C; d 2.75. The melt is orange.

Extremely sensitive to moisture, which rapidly converts it to the white $NbOCl_3$ and then to $Nb_2O_5 \cdot x\,H_2O$; hence it cannot be handled in air without marked decomposition. Reacts vigorously with water (dec.); dissolves without decomposition in ethanol, ether and, by an unknown mechanism, also in very concentrated hydrochloric and oxalic acid solutions.

$TaCl_5$

I.

$$\underset{181.0}{Ta} + \underset{56\,l.}{5/2\,Cl_2} = \underset{358.2}{TaCl_5}$$

The preparation from the elements is exactly the same as in method I for $NbCl_5$. When Ta powder is used, the reaction starts at 170°C and is complete in a few hours at 250°C.

DropBooks

II. $$\underset{441.9}{Ta_2O_5} + 5\,\underset{594.9}{SOCl_2} = 2\,\underset{716.5}{TaCl_5} + 5\,\underset{320.3}{SO_2}$$

A mixture of 2.6 g. of Ta_2O_5 and 5.5 ml. of $SOCl_2$ (threefold excess) is heated for 6 hours in a bomb tube at 230-240°C. The preparation of the starting materials and the procedure are exactly the same as for $NbCl_5$, method II. The reaction yields a liquid solution of $TaCl_5$ in $SOCl_2$ from which $SOCl_2$ is removed by distillation in the apparatus shown in Fig. 309, while the $TaCl_5$ is resublimed.

III. $$\underset{441.9}{Ta_2O_5} + 5\,\underset{769.2}{CCl_4} = 2\,\underset{716.5}{TaCl_5} + 5\,\underset{494.6}{COCl_2}$$

The reaction is carried out exactly as for $NbCl_5$, method III, the mixture being heated to 300-320°C.

Alternate methods: a) Methods IV and V for the preparation of $NbCl_5$ can be applied to $TaCl_5$ in exactly the same manner. Since (in contrast to $NbOCl_3$) no tantalum oxychloride is formed, the products are fairly pure.

b) From Ta and HCl at about 400°C [R. C. Young and C. H. Brubaker, J. Amer. Chem. Soc. 74, 4967 (1952)].

c) According to Chaigneau, the reaction between Ta_2O_5 and $AlCl_3$ reported by Ruff and Thomas is nearly quantitative when the reactants are used in the following proportions:

$$\underset{1825.7}{3\,Ta_2O_5} + \underset{1333.5}{10\,AlCl_3} = \underset{2149.4}{6\,TaCl_5} + \underset{509.8}{5\,Al_2O_3}$$

Before use, the $AlCl_3$ should be purified by vacuum sublimation. The reactants are sealed under vacuum into a tube of high-melting glass. After heating for 48 hours at 400°C, the $TaCl_5$ product can be separated from the Al_2O_3 by vacuum sublimation at 200°C. According to Schäfer, Göser and Bayer, reaction mixtures with a different composition (2 Ta_2O_5 + 5 $AlCl_3$) yield AlOCl as the residue. Mixtures of Nb_2O_5 and $AlCl_3$ usually yield only mixtures of $NbCl_5$ and $NbOCl_3$ [O. Ruff and F. Thomas, Z. anorg. allg. Chem. 146, 1 (1925); H. Schäfer, C. Göser and L. Bayer, Z. anorg. allg. Chem. 263, 67 (1950); M. Chaigneau, Comptes Rendus Hebd. Séances Acad. Sci. 243, 957 (1956)].

PROPERTIES:

Colorless crystalline needles; yellow when contaminated by $NbCl_5$ (even 1% $NbCl_5$ imparts a definite yellow color) or tungsten chlorides. M.p. 216.2°C, b.p. 239°C; d 3.68. Very sensitive to moisture; decomposed by H_2O and even by concentrated HCl, separating tantalic acid. Soluble in absolute ethanol.

REFERENCE:

I. K. R. Krishnaswami. J. Chem. Soc. (London) 1930, 1277; K. M. Alexander and F. Fairbrother. J. Chem. Soc. (London) 1949, 223; W. Littke. Thesis, Univ. of Freiburg i. Br., 1961.
II. H. Hecht, G. Jander and H. Schlapmann. Z. anorg. Chem. 254, 255 (1947); J. Wernet. Z. anorg. allg. Chem. 267, 213 (1952); experiments carried out in the Chemical Laboratory of the University, Freiburg i. Br., 1951.
III. O. Ruff and F. Thomas. Z. anorg. allg. Chem. 156, 213 (1926); H. Schäfer. Z. Naturforsch. 3b, 376 (1948); H. Schäfer and C. Pietruck. Z. anorg. allg. Chem. 264, 1 (1951); 267, 174 (1951).

Niobium Oxytrichloride

$NbOCl_3$

I. $$\underset{270.2}{NbCl_5} + \underset{11.2\ l.}{{}^1/_2 O_2} = \underset{215.3}{NbOCl_3} + Cl_2$$

About 2 g. of $NbCl_5$ is allowed to sublime from a side arm into a reactor tube which is approximately 20 mm. I.D. To promote good distribution of the $NbCl_5$, the tube contains a small amount of washed and dried glass wool. A slow stream of dry O_2 (1–2 liters/hour) is passed through while the tube which is heated to 150°C by means of a tubular electric furnace. About 80% of the $NbCl_5$ reacts in 2 hours. The remainder sublimes unchanged into the cold section of the tube, from which it is driven back (vacuum) and then again treated with O_2. In this manner, nearly complete conversion is achieved; the nascent $NbOCl_3$ is sublimed in an O_2 stream at 200°C to that section of the tube which is kept at 100°C. It deposits there as a dense crystal rosette. The material is discharged from the tube and handled under completely anhydrous conditions.

II. Prepared in a sealed tube according to the reaction:

$$\underset{265.8}{Nb_2O_5} + \underset{356.9}{3\,SOCl_2} = \underset{430.6}{2\,NbOCl_3} + \underset{192.2}{3\,SO_2}$$

The reaction proceeds exactly according to the stoichiometry shown by the equation. The method used for preparing the reactants is the same as that described for the preparation of $NbCl_5$ (p. 1303). A recommended charge for a normal bomb consists of 13.3 g. of Nb_2O_5 (1/20 mole) and 10.9 ml. of $SOCl_2$, prestirred into a paste.

It is important that the reactants be intimately mixed before they are heated, because otherwise the $SOCl_2$ will react preferentially with the outer part of the oxide mass to form $NbCl_5$, while a large portion of the oxides will remain unreacted. The mixture is heated for about 6 hours at 200°C. After cooling, well-formed crystals of $NbOCl_3$ (fine needles) are found in the lower part of the tube. Purification (by sublimation) and isolation of the $NbOCl_3$ must be done carefully: temperatures should be held below 350°C to prevent decomposition into Nb_2O_5 and $NbCl_5$. This operation is best carried out in the apparatus of Fig. 309.

III. $$\underset{265.8}{Nb_2O_5} + 3\,\underset{810.6}{NbCl_5} = 5\,\underset{1076.5}{NbOCl_3}$$

A glass tube is filled under vacuum with 0.3 g. of Nb_2O_5 and 3 g. of $NbCl_5$ (a very large excess), with the two compounds placed at opposite ends of the tube. The inclined tube is then heated in a temperature gradient (Nb_2O_5 350°C/liquid $NbCl_5$ 210°C). After 12 hours, white crystalline needles of $NbOCl_3$ deposit in the center of the tube. Unreacted $NbCl_5$ is then removed by heating the tube in a 200/20°C temperature gradient. The $NbOCl_3$ is isolated under a blanket of dry, inert gas.

Alternate methods: a) The $NbOCl_3$ is often a by-product of preparative reactions for $NbCl_5$ [e.g., $Nb_2O_5 + CCl_4$, D. E. Sands, A. Zalkin and R. F. Elson, Acta Crystallogr. 12, 21 (1959)]. The separation from $NbCl_5$ can be achieved by repeated fractional sublimation under vacuum or in an O_2 stream at temperatures below 350°C.

b) The product can also be prepared by thermal decomposition of $NbCl_5$ etherate at 90°C. [F. Fairbrother, A. H. Cowley and N. Scott (1959)].

PROPERTIES:

Colorless, often crystallizes in very fine needles. Vapor pressure: 10 mm. (234°C); 760 mm. (335°C). Disproportionates into Nb_2O_5 (or Nb_9O_7Cl) and $NbCl_5$ above 350°C. Best purified by vacuum sublimation at 200°C. Very sensitive to moisture; decomposed by H_2O. Tetragonal crystals.

REFERENCE:

I. P. Süe, Bull. Soc. Chim. France [5] 6, 830 (1939); F. Fairbrother, A. H. Cowley and N. Scott, J. Less-Common Metals 1, 206 (1959).

II. H. Hecht, G. Jander and H. Schlapmann, Z. anorg. Chem. 254, 260 (1947); J. Wernet, Z. anorg. allg. Chem. 276, 213 (1952).

III. H. Schäfer and F. Kahlenberg, Z. anorg. allg. Chem. 305, 327 (1960).

Niobium (III) Bromide

$NbBr_3$

$$\underset{492.5}{NbBr_5} + \underset{22.4\ l.}{H_2} = \underset{332.7}{NbBr_3} + \underset{161.8}{2\,HBr}$$

The apparatus of Fig. 310, containing boat *s* with the niobium metal, is dried in a stream of very pure N_2 at 200°C. Furnace o_1 is then heated to 450°C and dry Br_2 vapor is introduced in an N_2 stream. The nascent $NbBr_5$ condenses at *a*.

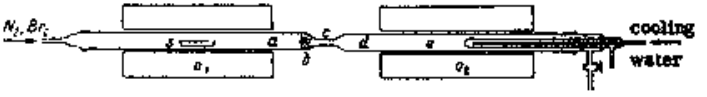

Fig. 310. Preparation of niobium (III) bromide. *s*) boat containing niobium metal; *b*) asbestos wool; o_1, o_2) electric furnaces.

After complete bromination, the bromide is sublimed in a pure N_2 stream at 270°C, passing through glass wool plug *b* and the constriction *c* into section *d*. Then, a stream of high-purity H_2 is introduced and $NbBr_5$ is allowed to sublime slowly into tube section *e*, kept at 500° by means of furnace o_2. It deposits on the tube wall as a shiny black crust and as a black cone on the cold finger. The tube is opened and the product is removed under a protective N_2 blanket. The outer crusts are not air-sensitive and are insoluble in H_2O. On the other hand, the cones deposited in the inner part of the apparatus decompose rapidly in the presence of moist air.

PROPERTIES:

Black, with varying air sensitivity, depending on preparative conditions. Almost completely resistant to H_2O and dilute acids. Decomposed by concentrated H_2SO_4 and HNO_3. Insoluble in organic solvents. Can be sublimed in a high vacuum (10^{-4} mm.) at about 400°C. Thermal decomposition into $NbBr_5$ and Nb begins at 900°C.

The $TaBr_3$ and the $TaBr_2$ can be obtained in the same manner as $NbBr_3$, starting from $TaBr_5$ and H_2 at 700°C; however, the purity and the yield are lower [R. C. Young and T. J. Hastings, J. Amer. Chem. Soc. 64, 1740 (1942)].

The $NbBr_2$ can be prepared from $NbBr_5$ and activated H_2 at 200°C; see preparation of $TaBr_4$, p. 1310 [V. Gutmann and E. Tannenberger, Monatsh. Chem. 87, 769 (1956)].

REFERENCE:

G. H. Brubaker and R. C. Young. J. Amer. Chem. Soc. 73, 4179 (1951).

Tantalum (IV) Bromide

$TaBr_4$

$$\underset{580.5}{TaBr_5} + H = \underset{500.8}{TaBr_4} + HBr$$

The horizontal reaction tube of high-melting glass (about 3 cm. I.D. and 50 cm. long) shown in Fig. 311 is heated in vacuum, and a boat containing $TaBr_5$ is introduced under anhydrous conditions. High-purity, dry H_2 is passed through the tube at a rate of about one liter per hour.

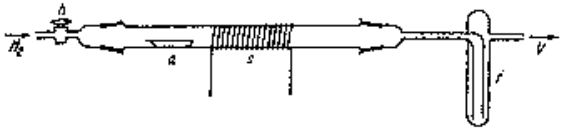

Fig. 311. Preparation of tantalum (IV) bromide. *a*) boat containing $TaBr_5$; *f*) cold trap; *h*) grooved stopcock for fine flow regulation; *s*) induction coil; *v*) vacuum.

A pressure of 4-6 mm. is maintained in the tube by means of the grooved stopcock *h*, which regulates the vacuum *v*. A glow discharge is produced by coil *s*, which consists of 16 turns of copper wire (2 mm. O.D.) on the outside of the tube; a high-frequency current of 4000 kilocycles/second is applied to the coil, which consumes about 20 watts. The glass wall temperature at the coil is about 180-200°C. The tube section containing $TaBr_5$ is heated; the $TaBr_5$ is slowly vaporized and reacts with the H_2 activated in the glow discharge zone. The nascent $TaBr_4$ is deposited on the tube wall in this zone. Unreacted $TaBr_5$, which condenses on the cooler portions of the tube, can be driven back into the reaction zone and reduced by moving the induction coil to another spot. The reaction of 0.8 g. of $TaBr_5$ is complete within 3 hours. The tube is allowed to cool and the product is scraped off the tube wall under anhydrous conditions.

PROPERTIES:

Black powder with steel-blue tinge. Slightly hygroscopic. Disproportionates to $TaBr_5$ and $TaBr_3$ at 300°C under vacuum. Yields a brown solution and an insoluble residue with H_2O.

REFERENCE:

V. Gutmann and H. Tannenberger. Monatsh. Chem. 87, 769 (1956).

Niobium (V) and Tantalum (V) Bromides

$NbBr_5$, $TaBr_5$

I. $Nb + {}^3/_2Br_2 = NbBr_5$; $Ta + {}^3/_2Br_2 = TaBr_5$

92.9 399.6 492.5 181.0 399.6 580.5

Pure, dry N_2 is saturated with Br_2 in a washing bottle or a saturation tube *s* (Fig. 312); the gas mixture is then passed over Nb or Ta metal contained in the horizontal reactor tube *r* made of quartz or high-melting glass. The metal may be either powder or solid.

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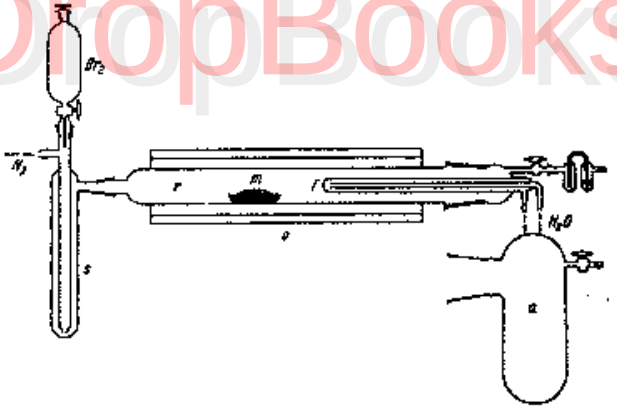

Fig. 312. Preparation of niobium (V) and tantalum (V) bromides. *a*) receiver; *f*) cold finger; *m*) boat containing the metal; *o*) tubular electric furnace; *r*) reactor tube; *s*) saturation tube.

First, the air is completely removed from the reactor. Then the section of the tube containing the metal is heated by a coil

wound directly on the reactor, or by a tubular electric furnace *a*. If Nb powder is used, then bromide formation begins at 90°C; with solid Nb, it starts at 195°C and with Ta powder at 155°C; it is complete in a few hours at 230–250°C. The nascent bromide sublimes onto cold finger *f*. When larger quantities are desired, large-diameter receiver *a* is attached to the end of the reactor. The extremely hygroscopic bromide should be removed from the apparatus while the latter is in a dry box (Part I, p. 71).

II. $3\,Nb_2O_5\,(3\,Ta_2O_5) + 10\,AlBr_3 = 6\,NbBr_5\,(6\,TaBr_5) + 5\,Al_2O_3$
797.5 1325.7 2667.3 2954.9 3483.2 509.8

In the method of Chaigneau, the mixture of pentoxide and $AlBr_3$, in proportions indicated by the above equation, is sealed under vacuum into a Pyrex glass tube (before use, the $AlBr_3$ is purified by vacuum sublimation). The tube is heated for 24 hours at 200°C, and allowed to cool; the small amounts of Br_2 formed in the process and residual $AlBr_3$ are vacuum-sublimed at 140°C. The pure pentahalide is then separated from the Al_2O_3 by vacuum sublimation at 240°C, yielding large crystals.

III. $Nb_2O_5\,(Ta_2O_5) + 3\,C + 6\,Br_2 = 2\,NbBr_5\,(2\,TaBr_5) + COBr_2 + 2\,CO_2$
265.8 441.9 36.0 959.0 985.0 1161.1 187.8 88.0

The bromides are prepared by a method similar to that presented for $NbCl_5$ (or $TaCl_5$) (method IV). An intimate mixture of the pentoxide with very pure charcoal (preferably sugar charcoal) is heated in a stream of inert gas (CO_2, N_2) carefully prepurified to remove traces of O_2 and H_2O and saturated with dry Br_2 in a wash bottle. There is a possibility of a side reaction leading to the oxybromide in the case of Nb_2O_5; however, this does not happen with Ta_2O_5. Wiseman and Gregory report a reaction temperature of 700–860°C in the case of Ta_2O_5. The final product is resublimed under an inert gas or, better, in a high vacuum (190–200°C); because of its high sensitivity to moisture, it should be handled only under anhydrous conditions.

Alternate methods: *a*) Reaction of the pentoxide with CBr_4 (analogous to that with CCl_4, see p. 1306) in a sealed tube yields pure $TaBr_5$ (in the case of Ta_2O_5) according to the equation: $Ta_2O_5 + 5\,CBr_4 = 2\,TaBr_5 + 5\,CO + 5\,Br_2$. The reactant mixture is heated for 7 days at 200°C, the gases formed are allowed to escape and $TaBr_5$ is vacuum-sublimed at 300°C. The yield is only about 70%. The corresponding reaction with Nb_2O_5 does not yield pure $NbBr_5$; instead, mixtures are formed [M. Chaigneau, Comptes Rendus Hebd. Séances Acad. Sci. 248, 3173 (1959)].

b) The $TaBr_5$ can also be obtained from Ta and HBr at 375°C [R. C. Young and C. H. Brubaker, J. Amer. Chem. Soc. 74, 4967 (1952)].

PROPERTIES:

$NbBr_5$: red crystals; m.p. 265.2°C, b.p. 361.6°C.
$TaBr_5$: yellow crystals; m.p. 265.8°C, b.p. 348.8°C, d 5.0.
Both compounds are very sensitive to hydrolysis, very soluble in ethanol (with a chemical reaction), and somewhat soluble in CCl_4.

REFERENCES:

I. M. Alexander and F. Fairbrother, J. Chem. Soc. (London) 1949, 223; D. H. Nowicky and I. E. Campbell in: H. S. Booth, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 130; R. F. Holsten, J. Phys. Chem. 62, 126 (1958); K. R. Krishnaswami, J. Chem. Soc. (London) 1930, 1277; C. H. Brubaker and R. C. Young, J. Amer. Chem. Soc. 73, 4179 (1951); W. Littke, Thesis, Univ. of Freiburg i. Br., 1961.
II. M. Chaigneau, Comptes Rendus Hebd. Séances Acad. Sci. 243, 957 (1956).
III. W. K. van Haagen, J. Amer. Chem. Soc. 32, 729 (1910); W. H. Chapin and E. F. Smith, J. Amer. Chem. Soc. 33, 1499 (1911); E. L. Wiseman and N. W. Gregory, J. Amer. Chem. Soc. 71, 2344 (1949).

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Niobium Oxytribromide

$NbOBr_3$

I. $$\underset{265.8}{Nb_2O_5} + \underset{995.0}{3\,CBr_4} = \underset{897.3}{2\,NbOBr_3} + \underset{67.2\ l.}{3\,CO} + \underset{67.2\ l.}{3\,Br_2}$$

A stoichiometric mixture of Nb_2O_5 and CBr_4 is heated for 24 hours at 200°C in an evacuated, sealed tube. The tube is opened at its thin, drawn-out end, and the gases present are allowed to escape. The $NbOBr_3$ is then purified by vacuum-sublimation at 300°C. The yield is nearly quantitative.

II. $$\underset{492.5}{NbBr_5} + \underset{11.2\ l.}{{}^1/_2O_2} = \underset{348.7}{NbOBr_3} + Br_2$$

The apparatus is similar to that used for preparation of $NbOCl_3$ (method I); the $NbBr_5$ is heated in an O_2 stream at 150°C. About 1 hour is necessary for 1 g. of $NbBr_5$. The $NbOBr_3$ product is then vacuum-sublimed at 180°C into another section of the reactor and kept there at 90°C. A dense crystal deposit is obtained. The final $NbOBr_3$ must be isolated and handled under completely anhydrous conditions.

Alternate methods: a) Reaction of Nb_2O_5 with C and Br_2 at 540°C.

b) Decomposition of $NbBr_5$ etherate at 112°C [F. Fairbrother, A. H. Cowley and N. Scott (1959)].

$TaOBr_3$ can be prepared from $TaBr_5$ and O_2 at 200°C via method II, but cannot be sublimed without decomposition.

PROPERTIES:

Yellow-brown; moisture sensitive, fumes in moist air. Thermal decomposition into Nb_2O_5 and $NbBr_5$ begins above 320°C.

REFERENCES:

I. M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. 248, 3173 (1959).

II. F. Fairbrother, A. H. Cowley and N. Scott. J. Less-Common Metals 1, 206 (1959).

Niobium (IV), Niobium (III) and Niobium (II) Iodides

NbI_4, NbI_3, NbI_2

NbI_5 =	NbI_4 +	$\frac{1}{2}I_2$;	NbI_5 =	NbI_3 +	I_2
737.5	600.5	11.2 *l.*	737.5	473.6	22.4 *l.*

NbI_4

A tube, dried by fanning with a flame and prepared for evacuation and melt-sealing, is charged with a small amount of NbI_5 under completely anhydrous conditions.

The tube is then sealed in a high vacuum and the end containing NbI_5 is heated to 270°C while the reactor is in a horizontal position. The liberated iodine collects at the other end, which is kept at a temperature of about 35°C ($p[I_2]$ = 0.8 mm.). The reaction time is about 48 hours. A residue of NbI_4 remains on the spot where the starting NbI_5 was placed; it can be sublimed at about 300°C under the above-indicated I_2 pressure.

NbI_3

Either NbI_5 or NbI_4 is heated under vacuum in a horizontal sealed tube, as described in the preparation of NbI_4. The higher iodide is heated to 425–430°C and the tube end in which the liberated I_2 collects is kept at 40°C. Reaction time is 48 hours. The NbI_3 formed can be resublimed in the tube at 450–500°C (partial decomposition).

NbI_3

$$\underset{473.6}{NbI_3} + \underset{11.2\,l.}{{}^1/_2H_2} = \underset{348.7}{NbI_2} + \underset{22.4\,l.}{HI}$$

A boat containing NbI_3 is heated in a stream of pure H_2. The reaction begins at 300°C and is complete in a few hours at 400°C. Higher temperatures should be avoided to prevent reduction to Nb metal or Nb hydride (these reactions start above 400°C).

PROPERTIES:

NbI_4: dark-gray crystalline oblong leaflets or thin needles; metallic luster. Soluble in H_2O and dilute hydrochloric acid.

NbI_3: insoluble in H_2O or conc. HCl.

NbI_2: gray-black. Insoluble in organic solvents; slowly hydrolyzed by H_2O. d 5.18.

REFERENCE:

M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. 242, 263 (1956); 245, 1805 (1957); J. D. Corbett and P. X. Seabaugh. J. Inorg. Nuclear Chem. 6, 207 (1958).

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Niobium (V) Iodide

NbI_5

$$\underset{92.9}{Nb} + \underset{634.6}{{}^5/_2I_2} = \underset{737.5}{NbI_5}$$

A vertical tube of Vycor or Pyrex glass (I.D. approximately 23 mm., wall thickness 2.5 mm.) is charged with 4–12 g. of Nb metal (either solid or powder). A dense glass wool plug is placed over the charge and approximately 20 cm. from the closed tube end, followed by a 20% excess of pure, resublimed I_2 powder. The tube and its contents are thoroughly degassed in a high vacuum and melt-sealed under vacuum. Then the reactor is placed in a slightly inclined position (with the Nb metal at the higher and the I_2 at the lower end) and heated by means of two separate tubular electric furnaces (these meet at the center of the tube). The niobium is heated to 300°C and the I_2 first to 180°C and then to 250°C. The reaction is nearly quantitative after 10–15 hours and NbI_5 crystals collect in the transition zone between the two temperature regions. The yields are lower with Nb powder than with solid Nb. The reactor is broken at the center, the NbI_5 is

removed under anhydrous conditions (e.g., in a dry box, see Part I, p. 71), and repeatedly rinsed with dry petroleum ether (under N_2) until the adhering I_2 is removed and the petroleum ether stays colorless. The traces of petroleum ether are evaporated in vacuum.

According to Corbett and Seabaugh, this synthesis can also be carried out in a V-shaped, closed reactor tube.

The method of reacting a pentoxide with AlI_3, used successfully for the preparation of TaI_5, yields only impure NbI_5 when Nb_2O_5 is the starting material [M. Chaigneau, Comptes Rendus Hebd. Séances Acad. Sci. 242, 263 (1956)].

Alternate method: Repeated distillation of $NbBr_5$ in an HI stream (a pure product is not readily obtained, however) [W. M. Barr, J. Amer. Chem. Soc. 30, 1568 (1908); W. K. van Haagen, J. Amer. Chem. Soc. 32, 729 (1910)].

PROPERTIES:

Yellow leaflets or needle-shaped crystals with a brass luster. Sublimes without decomposition only under considerable I_2 pressure. Very sensitive to moisture; decomposed by H_2O, forming HI.

REFERENCE:

F. Körösy. J. Amer. Chem. Soc. 61, 838 (1939); K. M. Alexander and F. Fairbrother. J. Chem. Soc. (London) 1949, 2472; R. F. Rolsten. J. Amer. Chem. Soc. 79, 5409 (1957); J. D. Corbett and P. X. Seabaugh. J. Inorg. Nuclear Chem. 6, 207 (1958); W. Littke. Thesis, Univ. of Freiburg i. Br., 1961.

Tantalum (V) Iodide

TaI_5

I.

$$\underset{180.9}{Ta} + \underset{634.6}{5/2\,I_2} = \underset{815.5}{TaI_5}$$

The procedure corresponds exactly to that described for NbI_5. The tube end containing the Ta metal is heated to 300°C and that containing the I_2 first to 180, then to 250°C. The reaction is complete in 10–15 hours.

II.

$$\underset{1325.7}{3\,Ta_2O_5} + \underset{4077.1}{10\,AlI_3} = \underset{4893.0}{6\,TaI_5} + \underset{509.8}{5\,Al_2O_3}$$

In this method of Chaigneau, a stoichiometric mixture of Ta_2O_5 and AlI_3, in a Pyrex glass tube, is heated in vacuum for 24 hours

at 230°C. The tube section containing the reaction mixture (which by then is black) is heated further to 350°C and finally to 520°C. The TaI_5 sublimes (nearly theoretical yield) into the colder end of the tube, where it deposits as crystals.

PROPERTIES:

Shiny black rhombic crystals, subliming at 543°C. Vapor pressure: 7.6 mm. (320°C); 96 mm. (420°C); 421 mm. (500°C). d 5.80. Very sensitive to moisture.

REFERENCE:

I. F. Körösy. J. Amer. Chem. Soc. 61, 838 (1939); K. M. Alexander and F. Fairbrother. J. Chem. Soc. (London) 1949, 2472; R. F. Rolsten. J. Amer. Chem. Soc. 80, 2952 (1958); W. Littke. Thesis, Univ. of Freiburg i. Br., 1961.
II. M. Chaigneau. Comptes Rendus Hebd. Séances Acad. Sci. 242, 263 (1956).

Niobium (II) Oxide

NbO

I.

$$\underset{124.9}{NbO_2} + \underset{92.9}{Nb} = 2\,\underset{217.8}{NbO}$$

A mixture of NbO_2 and Nb metal is pulverized to as small a size as possible and then compressed into small pellets which are heated for 10–20 minutes at 1600–1700°C in an atmosphere of very pure Ar or in a high vacuum. The best support for these pellets is Nb sheet; however, the pellets should touch this sheet only at a very few points.

II. NbO can also be prepared via a prolonged reduction of higher niobium oxides with H_2. An especially thorough prepurification and predrying of the hydrogen is essential. The reaction is carried out at 1300–1750°C. The reduction of 0.5 g. of NbO_2 to NbO takes about 60 hours at 1350° and about 15 hours at 1700°C. It is important to follow the progress of the reduction via a periodic check on the weight of the reactants; this is because the reaction also readily yields Nb metal in addition to NbO. The metal may start to accumulate after the run is in progress for some time and, in the presence of the unavoidable trace impurities in H_2, may be converted into Nb_2N and Nb_2C.

PROPERTIES:

Formula weight 108.91. Gray, submetallic. d 7.30. Crystal structure: special type similar to B 1 (NaCl) type.

REFERENCE:

G. Grube, O. Kubaschewski and K. Zwiauer. Z. Elektrochem. 45, 885 (1939); O. Kubaschewski. Z. Elektrochem. 46, 284 (1940); G. Brauer. Z. anorg. allg. Chem. 248, 1 (1941).

Niobium (IV) Oxide

NbO_2

In this procedure, pure Nb_2O_5 is reduced in an H_2 stream at 1000–1200°C.

$$\underset{285.8}{Nb_2O_5} + \underset{22.4\ l.}{H_2} = 2\,\underset{249.8}{NbO_2} + \underset{18.0}{H_2O}$$

The reduction time for 1 g. of oxide (contained in a boat) is 1–2 hours. Weight control is necessary, since prolonged heating at high temperatures produces some further reduction to NbO.

PROPERTIES:

Formula weight 124.91. Black powder. d 5.9. Crystal structure: C 4 (rutile) type.

REFERENCE:

P. Klinger. Techn. Mitteil. Krupp, Forschungsber. 1939, p. 171; G. Grube, O. Kubaschewski and K. Zwiauer. Z. Elektrochem. 45, 885 (1939); G. Brauer. Z. anorg. allg. Chem. 248, 1 (1941).

Niobium (V) and Tantalum (V) Oxides

Nb_2O_5, Ta_2O_5

Commercial Nb_2O_5 and Ta_2O_5 are usually low-purity products; in particular, Nb_2O_5 often contains Ta_2O_5. They are frequently contaminated with Fe, Ti and Sn since these elements accompany Nb and Ta in the original minerals. The following methods for purifying the pentoxides are based on the assumption that the content of these impurities does not exceed a few percent.

I. PURIFICATION VIA THE CHLORIDE

a) The tantalum and the tin can be removed from commercial Nb_2O_5 (or Ta_2O_5) by converting the oxide into a chloride, followed by extraction or distillation. This method is limited to small quantities of reactants.

As we have shown in the preparation of $NbCl_5$ (or $TaCl_5$) (p. 1304) 1 g. of the oxide and 4 ml. of CCl_4 are placed in a common tubular bomb (which need not be evacuated), and chlorination is carried out while heating to 250–300°C. The sealed tube is then opened, and the solid pentachloride product is extracted five times by shaking with 5-ml. portions of CCl_4, followed by phase separation. This may be done in air provided the operation is carried out quickly. The $TiCl_4$ and $SnCl_4$ are very readily soluble in CCl_4, whereas the pentachlorides dissolve less readily and less rapidly (less than 10 mg. of chloride/1 ml. of CCl_4) and therefore remain as residues. The residues are then converted to the oxides with H_2O. Assuming complete chlorination prior to the extraction, the Ti and Sn content of the product oxides should be ≥ 0.05%.

b) Instead of leaching the $TiCl_4$ and $SnCl_4$ out of the chlorination product, the latter can be removed by vacuum sublimation at 0.1 mm. and 200°C (after the sealed tube is opened). In this procedure the subliming pentachlorides travel only a short distance within the tube before depositing in a cooler zone; however, the $TiCl_4$ and $SnCl_4$ are volatilized so completely that the pentoxides obtained by this procedure contain less than 0.05% of TiO_2 and SnO_2.

c) The following method, which can be used to purify Nb_2O_5 (but not Ta_2O_5), has the advantage over the previously described one that it can be used with larger quantities of reactants.

The following preliminary treatments may be used:

a) Nb_2O_5 is fused with $KHSO_4$; the melt is allowed to cool and, after the grinding, is treated with dilute H_2SO_4 and H_2O_2. The hydrated oxide is precipitated from the peroxide solution with SO_2 at the boiling point, the mixture is decanted, the supernatant is discarded and the aqueous slurry of the precipitate is used in further reactions.

b) Freshly precipitated hydrated oxide (or the Nb_2O_5-$KHSO_4$ melt) is directly dissolved in ammonium oxalate or tartaric acid and the resulting solution of the complex is used in further reactions.

c) A hydrochloric acid solution or suspension of the chlorination products ($NbCl_5$, $NbOCl_3$) may be the starting material.

Next, the solution (or suspension) is adjusted to a volume corresponding to a maximum concentration of 4 g. (or, even better, 2–3 g.) of Nb_2O_5/100 ml. and the solution is saturated, while ice-cooling and agitating, with HCl gas as described in detail in the preparation of $(NH_4)_2TiCl_6$, p. 1199 ff. The suspension, as well as

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the hydrated oxide precipitated during the treatment with HCl, eventually becomes clear when the solution is saturated with HCl; sometimes, however, the HCl treatment and the agitation must be quite long. Approximately three hours are required per 100 ml. Then 4 g. of solid NH_4Cl per 100 ml. is added and the mixture is agitated for approximately half an hour. The $(NH_4)_2TiCl_6$ and $(NH_4)_2SnCl_6$ precipitate up to their respective solubility limits (0.5 mg. of Ti and 0.4 mg. of Sn/100 ml.). The mixture is filtered through a small-pore fritted-glass filter (it is best to cool the filter externally with ice); the filtrate is diluted with four to five times its volume of H_2O and then hydrolyzed at the boiling point. The readily filtered hydrated oxide is then calcined to the oxide. A 70–80% yield of purified Nb_2O_5, containing less than 0.1% of TiO_2 or SnO_2, is obtained. The losses are due to the isomorphous occlusion of $(NH_4)_2NbOCl_5$ by the precipitated $(NH_4)_2TiCl_6$.

II. SEPARATION VIA THE OXALATE

Very pure niobium oxide can be obtained either from crude niobium oxide or from concentrated niobium oxide mixtures, provided the Ta_2O_5:Nb_2O_5 ratio is not greater than 1:4. The following method is used: Precipitated, moist hydrated oxide (equivalent to about 20 g. of anhydrous oxide) is repeatedly treated with fresh 200-ml. portions of a solution which is 2N in HCl and 5% in oxalic acid dihydrate. Each treatment involves heating the mixture for several hours on a bath at 60–70°C with stirring, followed by decantation. Most of the Ta remains in the insoluble residue, which also becomes concentrated in Ti and W; the nearly pure Nb goes into solution, always accompanied by Sn. The combined solutions are evaporated to dryness, and the residue calcined to decompose the oxalic acid. The calcination residue is rather pure Nb_2O_5, containing only about 1% Ta_2O_5 plus some alkali stemming from the starting material.

This fairly pure Nb_2O_5, in the form of precipitated hydrated oxide, may again be subjected to the same leaching operation, which gives a virtually Ta-free oxide.

III. SEPARATION BY EXTRACTION

The extraction of aqueous hydrofluoric solutions of the pentoxides with immiscible ketones can be used with very impure starting materials. In this case there is no restriction on the permiseible Nb:Ta ratio. In this extraction, the aqueous phase contains HF and either HCl, HNO_3 or H_2SO_4; the best purification efficiency is obtained with HNO_3 and H_2SO_4. The coefficients for partition of Nb and Ta between the two phases depend to a large

extent on the acid concentration. The extracting agents may be methyl isobutyl ketone (MIBK) or cyclohexanone. All equipment must be made of an HF-resistant material (polyethylene or polyvinyl chloride).

The pentoxide (or a mixture of pentoxides) is dissolved in strong hydrofluoric acid and the resulting solution adjusted, by addition of H_2SO_4, to a concentration of 100 g. of pentoxide/liter, 5.6 N HF and 9 N H_2SO_4. This solution is extracted twice with half its volume of MIBK. The combined ketone extracts contain virtually all of the Nb and Ta originally present and are free of other metals. The organic phase is then extracted with aqueous acid as follows.

a) When the starting material is either Nb_2O_5 or an Nb-rich mixture, the organic phase is shaken with the same volume of an aqueous solution that is 3 N in H_2SO_4 and 1 N in HF. This aqueous phase then contains 90% of the Nb, but less than 0.1% of Ta. A second extraction of the ketone phase with fresh acid solution gives a second, smaller Nb fraction of lower purity. A small amount of high-purity Ta remains in the organic phase.

b) When the starting material is Ta_2O_5 or a Ta-rich mixture, the organic phase stemming from the first extraction is shaken with the same volume of an aqueous acid solution which is 4.5 N in H_2SO_4 and 2.8 N in HF, thus removing all of the Nb together with a small amount of Ta. The remaining ketone solution contains most of the Ta (99.9% purity).

Pure Nb or Ta is obtained from the ketone solutions by extraction with pure H_2O. The pentoxide, dissolved in the aqueous (more or less acidic) final solutions, is then precipitated with ammonia.

In special cases or when the starting materials contain a moderate Nb:Ta ratio the procedure can be modified. These modifications are summarized in the following table.

Extraction of Nb and Ta with Methyl Isobutyl Ketone (MIBK)

Extraction system	Optimum extraction for Ta alone (from the aqueous phase)	Optimum extraction for Nb or Nb + Ta (from the aqueous phase)
$(HF + HNO_3)$/MIBK	0.5 N HF + 1 N HNO_3	7 N HF + 5 N HNO_3
$(HF + H_2SO_4)$/MIBK	1 N HF + 3 N H_2SO_4	5.6 N HF + 9 N H_2SO_4
(HF + HCl)/MIBK	3 N HF + 3 N HCl or 3 N HF	6.5 N HF + 7.2 N HCl

Alternate methods:

IV. FLUORIDE SEPARATION BY THE METHOD OF MARIGNAC

Fractional crystallization of K_2TaF_7 is accomplished by adding KF to hydrofluoric solutions of Nb and Ta, while K_2NbOF_5 accumulates in the mother liquor. This procedure is more suitable for a large-scale process than the laboratory [O. Hönigschmid and K. Wintersberger, Z. anorg. allg. Chem. 219, 161 (1934); C. W. Balke, Trans. Electrochem. Soc. 85, 89 (1944); G. S. Savchenko and Ya. V. Tananayev, Zh. Prikl. Khimii 19, 1093 (1946); 20, 385 (1947)].

V. TANNIN PRECIPITATION

Small amounts (about 1 g.) of very pure Nb_2O_5 and Ta_2O_5 can be obtained from the corresponding crude oxides via a simple fractional precipitation of oxalate complex solutions with tannin. The procedure is based on the analytical method of Schoeller (1937).

VI. SEPARATION WITH ION EXCHANGERS

The separation of Nb and Ta on an ion exchange column is promising but not yet sufficiently developed. The Nb and Ta products can be obtained in 99% purity from solutions which are 9 M in HCl and 0.05 M in HF [K. A. Kraus and G. D. Moore, J. Amer. Chem. Soc. 71, 3855 (1949); E. H. Huffman, G. M. Iddings and R. C. Lilly, J. Amer. Chem. Soc. 73, 4474 (1951); J. L. Hague, E. D. Brown and H. A. Bright, J. Res. Nat. Bur. Standards 53/4, 261 (1954); P. Münchow, Chem. Ztg. 84, 490, 527 (1960)].

PROPERTIES:

Nb_2O_5: White powder turning yellow on heating; insoluble in aqueous acids other than hydrofluoric. M.p. 1495°C. Crystallizes in various modifications; does not form well-defined hydrates.

Ta_2O_5: White powder; insoluble in aqueous acids other than hydrofluoric. M.p. 1872°C. Crystallizes in various modifications; forms no defined hydrates.

REFERENCES:

General: W. R. Schoeller, The Analytical Chemistry of Tantalum and Niobium, London, 1937; H. Schäfer, Angew. Chem. 71, 153 (1959); G. L. Miller, Tantalum and Niobium, London, 1959.

1. R. F. Weinland and L. Storz, Z. anorg. allg. Chem. 54, 223 (1907); H. Schäfer and C. Pietruck, Z. anorg. allg. Chem. 264, 106 (1951).

II. H. Schäfer, L. Bayer and C. Pietruck. Z. anorg. allg. Chem. 266, 140 (1951); J. Wernet, Z. anorg. allg. Chem. 267, 213 (1952).

III. K. B. Higbie and J. R. Werning. U. S. Bur. Min. Rep. Invest. No. 5239 (1956); E. L. Koerner, M. Smuts and H. A. Wilhelm. Meeting of Extractive Metallurgy Section of the A.I.Ch.E., Chicago, 1957; G. H. Faye and W. R. Inman. Canad. Dept. Min. Techn. Surv. Res. Rep. No. MD 210 (1957); J. L. Tews and S. L. May. U. S. Bur. Min. Rep. No. USBM-U-252 (1957); C. W. Carlson and R. H. Nielsen, J. Metals 12, 472 (1960).

Alkali Niobates and Tantalates

Either Nb_2O_5 or Ta_2O_5 is heated with an alkali hydroxide or alkali carbonate. Salts of differing composition are obtained, depending on the reactant ratios, the temperature, and workup of the reaction product. Systematic investigation has shown that the system alkali oxide–pentoxide contains a wide range of compounds.

The thoroughly dried starting Nb_2O_5 (or Ta_2O_5) and Li_2CO_3, Na_2CO_3 or K_2CO_3 are mixed in ratios calculated to give the desired final composition; the mixtures are heated in a crucible at a slowly increasing temperature (e.g., 100°C/hour) to insure a smooth reaction without loss of reactants. The best crucible material is Pt or (particularly for mixtures with high alkali concentrations) an 80% Au, 20% Pd alloy. The temperature is increased to just below the melting point of the mixture and kept at this point several hours; the mixture is then cooled and pulverized. The heating and pulverization are repeated an additional two times. An oxygen atmosphere is maintained over the crucible during the heating to prevent the product from splitting off oxygen.

In the preparation of the meta salts

$$\underset{285.8}{Nb_2O_5} + \underset{73.9}{Li_2CO_3}(\underset{106.0}{Na_2CO_3}, \underset{138.2}{K_2CO_3}) \rightarrow 2\,\underset{295.7}{LiNbO_3}(2\,\underset{327.8}{NaNbO_3}, 2\,\underset{360.0}{KNbO_3})$$

$$\underset{441.9}{Ta_2O_5} + \underset{73.9}{Li_2CO_3}(\underset{106.0}{Na_2CO_3}, \underset{138.2}{K_2CO_3}) \rightarrow 2\,\underset{471.8}{LiTaO_3}(2\,\underset{503.9}{NaTaO_3}, 2\,\underset{536.1}{KTaO_3})$$

the amount of alkali carbonate may be somewhat greater than that indicated by the 1:1 molar ratio (however, a 2:1 ratio should not be exceeded) and the reaction mixture may be extracted with warm H_2O. The meta salts remain as residues which dissolve only with difficulty. Larger single crystals of the meta salts can be obtained from a KF or KCl melt.

For information concerning polyniobates and polytantalates, see Part III, Section 3.

PROPERTIES:

Colorless, crystalline compounds.
The following phases are known:

Li_2O–Nb_2O_5:

3 $Li_2O \cdot Nb_2O_5$ (m.p. 1408°C); $Li_2O \cdot Nb_2O_5$ (m.p. 1253°C); $Li_2O \cdot 4\ Nb_2O_5$ (m.p. 1231°C, incongruent); $Li_2O \cdot 14\ Nb_2O_5$ (m.p. 1268°C, incongruent).

Na_2O–Nb_2O_5:

3 $Na_2O \cdot Nb_2O_5$ (m.p. 997°C); $Na_2O \cdot Nb_2O_5$ (m.p. 1422°C, polymorphous); $Na_2O \cdot 4\ Nb_2O_5$ (m.p. 1277°C, incongruemt); $Na_2O \cdot 14\ Nb_2O_5$ (m.p. 1309°C, incongruent).

K_2O–Nb_2O_5:

3 $K_2O \cdot Nb_2O_5$ (m.p. 950°C); $K_2O \cdot Nb_2O_5$ (m.p. 1039°C, incongruent); 2 $K_2O \cdot 3\ Nb_2O_5$ (m.p. 1163°C); $K_2O \cdot 3\ Nb_2O_5$ (m.p. 1234°C, incongruent); 3 $K_2O \cdot 22\ Nb_2O_5$ (m.p. 1279°C, incongruent); 6 $K_2O \cdot 7\ Nb_2O_5$ and 7 $K_2O \cdot 6\ Nb_2O_5$ (metastable, obtainable only by quenching).

K_2O–Ta_2O_5:

3 $K_2O \cdot Ta_2O_5$ (m.p. 1330°C); $K_2O \cdot Ta_2O_5$ (m.p. 1370°C, incongruent); $K_2O \cdot 2\ Ta_2O_5$ (m.p. 1520°C, incongruent); $K_2O \cdot 5\ Ta_2O_5$ (m.p. 1645°C, incongruent).

REFERENCES:

L. L. Quill. Z. anorg. allg. Chem. 208, 257 (1932); P. Süe. Comptes Rendus Hebd. Séances Acad. Sci. 198, 1696 (1934); P. Süe. Ann. Chimie [11] 7, 493 (1937); F. Windmaisser. Österr. Chemiker-Ztg. 45, 201 (1942); B. T. Matthias and J. P. Remelka. Phys. Rev. (2) 82, 727 (1951); E. A. Wood, Acta Crystallogr. 4, 353 (1951); A. Reisman, F. Holtzberg, M. Berkenblit, M. Berry and E. Banks. J. Amer. Chem. Soc. 77, 2115 (1955); 78, 719, 4514 (1956); 80, 37, 6503 (1958); 81, 1292 (1959).

Peroxyniobic and Peroxytantalic Acids

$HNbO_4 \cdot n\,H_2O$, $HTaO_4 \cdot n\,H_2O$

$HNbO_4 \cdot n\,H_2O$

$$\underset{694.4}{2\,K_2NbO_8 \cdot {}^1/_2H_2O} + \underset{294.2}{3\,H_2SO_4} + \underset{54.0}{3\,H_2O} = \underset{315.8}{2\,HNbO_4} + \underset{522.8}{3\,K_2SO_4} + \underset{204.1}{6\,H_2O_2}$$

Sulfuric acid (2 N, 10 ml.) is gradually added to a solution of 2 g. of **potassium** peroxyniobate in 50 ml. of H_2O. The precipitate

formed (caution: this precipitate redissolves readily if there is an excess of sulfuric acid) is filtered off and washed three to four times with H_2O, ethanol and ether. The yield is poor (about 1 g. of peroxyniobic acid, in the form of a light yellow powder).

$HTaO_4 \cdot n\,H_2O$

I. $$\underset{852.5}{2\,K_3TaO_8} + \underset{294.2}{3\,H_2SO_4} + \underset{491.8}{4\,H_2O} = \underset{}{2\,HTaO_4} + \underset{522.8}{3\,K_2SO_4} + \underset{204.1}{6\,H_2O_2}$$

A solution of 2 g. of K_3TaO_8 in 150 ml. of H_2O is prepared and an approximately equivalent quantity of dilute H_2SO_4 added all at once. The nascent precipitate is first centrifuged; it can then be filtered and washed with some H_2O, then with ethanol and ether.

II. $$\underset{441.9}{Ta_2O_5} + \underset{68.0}{2\,H_2O_2} = \underset{491.9}{2\,HTaO_4} - H_2O$$

Tantalic acid, freshly precipitated with ammonia from a solution containing 10 g. of K_2TaF_7, is treated with 50 ml. of H_2O and 50 ml. of 30% H_2O_2. The tantalic acid dissolves completely within a few hours, affording a transparent, opalescent liquid. The latter is treated with equal amounts of ethanol and saturated NaCl solution. The mixture, which at first stays clear, slowly deposits out a precipitate of peroxytantalic acid, which is filtered off the next day and dried with ethanol and ether.

PROPERTIES:

White substance. Gelantinous when wet, fine powder when dry. Ta : peroxy oxygen ratio = 1 : 1.

REFERENCES:

A. Sieverts and E. L. Müller. Z. anorg. allg. Chem. 173, 297 (1928); P. Melikow and L. Pissarjewsky. Z. anorg. Chem. 20, 344 (1899).

Potassium Peroxyniobate, Potassium Peroxytantalate

K_3NbO_8, K_3TaO_8

$$\underset{265.8}{Nb_2O_5} + \underset{336.6}{6\,KOH} + \underset{272.1}{8\,H_2O_2} = \underset{676.4}{2\,K_3NbO_8} + \underset{198.2}{11\,H_2O}$$

$$\underset{441.9}{Ta_2O_5} + \underset{336.6}{6\,KOH} + \underset{272.1}{8\,H_2O_2} = \underset{852.5}{2\,K_3TaO_8} + \underset{198.2}{11\,H_2O}$$

$K_3NbO_8 \cdot {}^1/_2\,H_2O$

I. A mixture of Nb_2O_5 (1 part) and KOH (6 parts) is fused in a silver crucible. The fused mass is dissolved in a minimum of

H_2O, a small amount of H_2O_2 is added and the mixture heated for a short while on the water bath. The solution is filtered to remove the black Ag particles, 9–10 moles of H_2O_2/mole of Nb_2O_5 is added, and the mixture is precipitated with an equal volume of ethanol. The precipitate is air-dried and washed with ethanol and ether; it is then redissolved in a mixture of three to four moles of H_2O_2 and 0.5 moles of KOH/mole of the Nb_2O_5 reactant and precipitated with 1–1.5 times its volume of ethanol. The precipitate is again dried with ethanol and ether.

II. The fusion step can be avoided by using freshly precipitated niobic acid or potassium niobate instead of Nb_2O_5. These compounds are dissolved in potassium hydroxide and the workup procedure is the same as that described in method I.

K_3TaO_8

Tantalic acid $Ta_2O_5 \cdot aq.$ is precipitated with ammonia from a tantalum solution (e.g., that of K_2TaF_7). The precipitate is suction-filtered and washed with a large quantity of H_2O. The gelatinous intermediate, which should not be allowed to age, is added to a solution of 20 g. of very pure KOH in 250 ml. of 3% H_2O_2 (made from "Perhydrol," Merck) until the solution is saturated. Cooling to 0°C causes separation of granular peroxytantalate crystals, which are suction-filtered and dried with ethanol and ether or in a vacuum desiccator over H_2SO_4.

The pure white crystals have a composition corresponding to K_3TaO_8; the yield is poor.

$K_3TaO_8 \cdot {}^1/_2 H_2O$

A mixture of Ta_2O_5 (5 g.) with three times the stoichiometric quantity of KOH is fused in a silver crucible. The product is allowed to cool and is then dissolved in 3% H_2O_2; any separated silver is filtered off. The solution is treated first with 20 times the stoichiometric quantity of H_2O_2 and then with an equal volume of ethanol. The precipitated, fine powder of the salt is suction-filtered and dried with ethanol and ether. Yield: 6 g. of pure white $K_3TaO_8 \cdot {}^1/_2 H_2O$.

REFERENCES:

A. Sieverts and E. L. Müller, Z. anorg. allg. Chem. 173, 297 (1928); C. W. Balke, J. Amer. Chem. Soc. 27, 1140 (1905); C. W. Balke and E. F. Smith, J. Amer. Chem. Soc. 30, 1637 (1908); P. Melikow and L. Pissarjewsky, Z. anorg. Chem. 20, 344 (1899).

Niobium and Tantalum Sulfides

I. FROM THE METALS

In general, the synthesis from the elements gives products of any desired composition. If the reactant ratios correspond exactly to the region in which a phase is homogeneous, the product is pure; otherwise, it is a mixture of phases.

A mixture of about 1–3 g. of solid Nb metal (or, better, Nb filings or powder) and that quantity of vacuum-distilled sulfur which will give the desired product composition is placed in a quartz tube, which is then evacuated. The mixture is heated slowly and then kept at 700–1000°C for two days. Under these conditions, dpending on the temperature used, either the high- or the low-temperature modification of a phase is obtained. Special conditions are required for some compounds (e.g., hexagonal NbS_2: 850°C < T < 1050°C, with the niobium placed in the hottest zone of the ampoule; rhombohedral $Nb_{1+x}S_2$: T > 800°C, niobium in the coldest zone of the ampoule).

In no case is the sulfur quantity absorbed greater than that corresponding to the formula NbS_2. No preparative methods are known as yet for NbS_3. Traces of this compound are formed during the preparation of other niobium sulfides. The heating of mixtures low in sulfur should be occasionally interrupted, the intermediate product repulverized and remixed, then replaced in the evacuated tube, and the heating continued.

The lower sulfides may also be obtained by homogenization of the corresponding mixtures of niobium sulfide + Nb. In addition, partial degradation of the higher sulfides by distilling off the sulfur in a high vacuum also yields lower sulfides. Another preparative method is based on the reaction of Nb with H_2S at temperatures between 550 and 900°C.

The tantalum sulfides are prepared by procedures based on the same principles. Since the phase relationships are less complicated, one has greater latitude in selecting the preparative conditions. The tantalum sulfide with the highest known S concentration is TaS_3, which can be obtained at 600°C.

II. FROM THE PENTOXIDES

Either Nb_2O_5 or Ta_2O_5 (2–10 g.) is placed in a loose layer in a porcelain reactor tube and exposed for three to six hours at 960–1300°C to a CS_2-saturated stream of H_2S; prior to entering the tube, the latter passes through a purification and drying train, as well as through a wash bottle containing CS_2 at 25–35°C. The reactor must be thoroughly purged of air prior to the run and air leaks must be avoided during the reaction. In particular, the

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H_2S must be air-free. The crude sulfides are then extracted with CS_2 to remove traces of precipitated S. The Nb product has the composition $NbS_{1.74}$, the Ta product $TaS_{2.0}$. It appears that no other compositions can be obtained by this method.

PROPERTIES:

The hexagonal NbS_2 and the rhombohedral $Nb_{1+x}S_2$ are blue-black, shiny crystalline compounds: NbS_2 single crystals 0.5 mm. in size can be obtained. The remaining niobium sulfides are dark-gray to black or dark-brown powders devoid of luster.

The TaS_2 consists of microscopically small leaflets, not appreciably volatile in vacuum up to 1100°C, whereas TaS_3 consists of a mass of loose, feltlike crystalline fibers which are always obtained when other modifications are heated for 14 days at 600°C. At 650°C, TaS_3 decomposes rapidly into TaS_2 and sulfur, which dissolves in the TaS_2. The sulfides are unaffected by hydrochloric acid and sodium hydroxide, but vigorously oxidized by hot concentrated H_2SO_4 or HNO_3.

Seven phases are known in the Nb-S system: "H-NbS" (temporary general designation, probably comprising two or more phases), hexagonal $Nb_{2-y}S_2$ ($0 < y < 0.3$) and the closely related hexagonal $Nb_{1-x}S_2$ ($0.3 < x < 0.43$), rhombohedral $Nb_{1+x}S_2$ ($0.12 < x < 0.5$), hexagonal NbS_2, rhombohedral NbS_3 and monoclinic NbS_3.

REFERENCES:

Nb-S: W. Biltz and A. Köcher, Z. anorg. allg. Chem. 237, 369 (1938); O. Hönigschmid and K. Wintersberger, Ibid. 219, 161 (1934); H. Biltz and W. Gonder, Ber. dtsch. chem. Ges. 40, 4963 (1907); G. Hägg and N. Schönberg, Ark. Kemi. 7, 371 (1954); Hörst Müller, Thesis, Univ. of Freiburg i Br., 1938; F. Jellinek, G. Brauer and H. Müller, Nature 185, 376 (1960).

Ta-S: W. Biltz and A. Köcher, Z. anorg. allg. Chem. 238, 81 (1938); H. Biltz and C. Kircher, Ber. dtsch. chem. Ges. 43, 1636 (1910); G. Hägg and N. Schönberg, Ark. Kemi 7, 371 (1954).

Niobium and Tantalum Nitrides

I. The pure Nb and Ta nitrides are prepared by synthesis from the elements. The reactant metals should be fine powders and should be degassed by heating in high vacuum. The N_2 must be completely free of O_2 and H_2O. With fine metal powders, the reaction temperature should be 1200°C; with filings or solid metal, it must be 1300 to 1500°C. Temperatures higher than these naturally increase the nitridation rate; however, because of

equipment limitations, they are employed only in the case in which the metal, in the form of wire, is clamped onto terminals and heated electrically in an N_2 atmosphere.

Hydrides of Nb and Ta can be used instead of the metal. The hydrides lose their hydrogen during the first stages of the reaction, affording an especially reactive, fine metal powder; this, in turn, permits lower reaction temperatures. In addition, very pure NH_3 may be used instead of N_2. The reaction of the metal with ammonia occurs at a temperature which is usually 300–400°C lower than that required for N_2.

a) Nitridation of thin metal wire can be achieved at temperatures between 1350 and 2800°C. This procedure, which uses nitrogen under pressure, always yields products with an N content corresponding to the upper limit, NbN. The rates of reaction are high but the amount of obtainable product is obviously small. Products with a low N content can be obtained by shortening the heating period and lowering the N_2 pressure; product homogeneity cannot be guaranteed, however.

b) To obtain nitrides from metal powder, the latter is placed in a sintered alumina boat inserted into a ceramic reactor tube. Because the nitrides are so extremely sensitive to oxygen, completely oxygen-free products can be obtained only if penetration of foreign gases is reduced by using the best, least porous ceramic reactor materials. Even these exhibit some porosity, however. The best method is to insert the reactor tube into another protective tube and fill the annular space between them with very pure N_2. The products vary in N content depending on the temperature and duration of nitridation, and can range up to NbN or TaN. To achieve high homogeneity and nitrogen contents, the mixture of reactants must be cooled from time to time, removed from the apparatus, reground to a fine powder, and nitridized again.

The best method for obtaining products of a given desired N content is synthesis starting from a homogeneous mixture of highly nitridized materials and metal powder. Such mixtures are homogenized by prolonged calcination at at least 1400°C (high vacuum or Ar atmosphere) with occasional cooling and regrinding of the calcined intermediate product.

II. Less pure niobium nitrides can be obtained from the oxide, carbon and nitrogen:

$$NbO_2 + 2C + {}^1/_2N_2 = NbN + 2CO.$$

An intimate mixture of NbO_2 and the stoichiometric quantity of ash-free carbon is calcined in a stream of very pure N_2 or NH_3 at 1250°C. The products probably still contain some O and C.

This method is completely unsuitable for the preparation of Ta nitrides because in this case the product contains considerable quantities of O and C.

The nitrides can also be obtained from the oxides and NH_3, provided the reaction time is sufficiently long.

PROPERTIES:

Dark products with submetallic appearance. Products with a high N content are yellowish-gray or brown, those with a low N content are dark gray. M.p.: NbN about 2000°C, TaN about 2800°C. The N_2 decomposition pressures become appreciable at temperatures exceeding 1400°C. Not attacked by acids. Readily and quantitatively converted to the pentoxides by moderate calcination in the presence of air (this is an analytical method).

The independent phases which exist in the Nb–N system correspond to the compositions $NbN_{1.00-0.87}$, $NbN_{0.78-0.76}$ and $NbN_{0.50-0.40}$; density of these ranges from 8.3 to 8.4.

The independent phases in the Ta–N system correspond to the compositions $TaN_{1.00}$ (d 13.8) and $TaN_{0.50-0.40}$ (d 15.4).

REFERENCE:

I a. K. Becker and F. Ebert, Z. Physik 31, 269 (1925); K. Moers, Z. anorg. allg. Chem. 198, 243 (1931); H. Rögener, Z. Physik 132, 446 (1952).

I b. C. Agte and K. Moers, Z. anorg. allg. Chem. 198, 233 (1931); G. Brauer, Z. Elektrochem. 46, 397 (1940); F. H. Horn and W. T. Ziegler, J. Amer. Chem. Soc. 69, 2762 (1947); G. Brauer and J. Jander, Z. anorg. allg. Chem. 270, 160 (1952); G. Brauer and K. H. Zapp, Z. anorg. allg. Chem. 277, 129 (1957); R. P. Elliot and S. Komjathy, Columbium Metallurgy Symposium, New York, 1960; G. Brauer and R. Esselborn, Z. anorg. allg. Chem. 309, 151 (1961).

II. E. Friederich and L. Sittig, Z. anorg. allg. Chem. 143, 308 (1925).

Niobium and Tantalum Phosphides

NbP_2, TaP_2, NbP, TaP

These phosphides are prepared by synthesis from the elements, either in a "Faraday apparatus" (see Part I, p. 76) or by

heating a mixture of metal powder and P in an Al_2O_3 crucible. In either case the reactor is a sealed, evacuated quartz tube.

$$\underset{92.9}{Nb} + \underset{31.0\ (62.0)}{P\ (2P)} = \underset{123.9\ (154.9)}{NbP\ (NbP_2)}$$

$$\underset{180.9}{Ta} + \underset{31.0\ (62.0)}{P\ (2P)} = \underset{211.9\ (242.9)}{TaP\ (TaP_2)}$$

In the "Faraday method," that end of the tube which contains the P is heated to 450–530°C, while that containing the metal is heated first to 750°C and then to 950 to 1100°C.

In the method which uses a mixture, a fast onset of the reaction sometimes leads to explosion of the sealed tube, particularly if the P content of the reactant mixture is high.

The lower phosphides can also be obtained by degradation of products higher in phosphorus. This is done in high vacuum at 650–800°C.

PROPERTIES:

Black to dark-gray substances; fairly resistant to common reagents, vigorous reaction only with conc. H_2SO_4; in the case of products high in phosphorus, also with conc. HNO_3. Completely decomposed by fusion with alkaline oxidizing agents. *d*: TaP_2 8.4; TaP 10.85.

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REFERENCE:

M. Zumbusch and W. Biltz. Z. anorg. allg. Chem. 246, 35 (1941); A. Reinecke, F. Wiechmann, M. Zumbusch and W. Biltz. Z. anorg. allg. Chem. 249, 1 (1942).

Niobium and Tantalum Carbides

I. a) Pure products must be synthesized from the elements.

$$\underset{92.9}{Nb} + \underset{12.0}{C} = \underset{104.9}{NbC}; \qquad \underset{180.9}{Ta} + \underset{12.0}{C} = \underset{192.9}{TaC}$$

Intimate mixtures of Nb or Ta metal powders (or Nb or Ta hydrides with carbon (as ash-free as possible) are placed in graphite boats or graphite crucibles and heated in a vacuum or in an H_2 atmosphere. Reaction temperatures vary between 1400 and 2100°C. When a tubular carbon furnace is used as the heat source and an H_2 stream as the protective gas, the carbon content of the mixtures should be 15–20% lower than stoichiometric; this is

because the heating causes the H_2 to react with the carbon of the furnace and the boat, and the resultant hydrocarbons supply the additional carbon needed to achieve the desired composition.

An additional purification of the carbide powder can be obtained by sintering (see TIN, p. 1233 f.). For purposes of presintering, the carbide powder is pressed into pellets which are embedded in loose carbide powder to protect them from chemical agents. These pellets are then presintered at a temperature of 2500–3000°C for about 15 minutes. The subsequent high-temperature sintering in argon at above 3000°C produces "self-purification" because of volatilization of impurities.

b) For small quantities of carbides, Nb (or Ta) wire is heated at temperatures exceeding 2500°C in an H_2 atmosphere which contains small amounts of hydrocarbon vapors. The presence of N_2 makes so little difference that up to 80% of the H_2 may be replaced by N_2. Suitable hydrocarbons are toluene, methane and acetylene. The nascent carbides formed may lose carbon at the high temperatures if the CH_4 content of the gas is less than about $^1/_4$%, or that of C_2H_2 is less than about $^1/_8$%.

II. The carbides can also be obtained by reacting the oxide with carbon.

$$\underset{124.9}{NbO_2} + \underset{36.0}{3\,C} = \underset{104.9}{NbC} + \underset{56.0}{2\,CO}$$

$$\underset{441.9}{Ta_2O_5} + \underset{84.1}{7\,C} = \underset{385.9}{2\,TaC} + \underset{140.1}{5\,CO}$$

The respective powder mixtures, in Mo or carbon boats, are reacted at 1250–2300°C in an H_2 stream. At 2300°C, a one-hour heating is recommended. When carbon tubes or boats are used as in method Ia, the mixture may be less than stoichiometric with respect to carbon. The products may be further purified via the above-cited sintering.

Alternate methods: Crystal growing procedures.

a) A carbon fiber is resistance-heated to above 2000°C with current. The fiber is in a "reaction lamp," which also holds thoroughly degassed $TaCl_5$ (this process cannot be used with Nb). The quantity of $TaCl_5$ needed is difficult to measure out (also, with excess chloride, free metal or lower carbides are formed on the incandescent fiber). At any rate, this process may be followed by carbidization in the presence of H_2 and a hydrocarbon vapor [W. G. Burgers and J. C. M. Basart, Z. anorg. allg. Chem. 216, 207 (1934)].

b) Carbide may also be deposited on a tungsten wire exposed at 1900–2300°C and 0.1 mm. Hg to an H_2 carrier gas containing small amounts of $TaCl_5$ ($NbCl_5$) and toluene vapor. However, this

carbide product will contain a large amount of free metal and must be subjected to a postcarbidization treatment [K. Becker and H. Ewest, Z. techn. Physik 11, 148 (1930); K. Moers, Z. anorg. allg. Chem. 198, 243 (1931)].

c) According to a patent [D. Gardner, U.S. Patent 2,532,285 (1946/50)], the pentachlorides can be reacted with H_2 and carbon derivatives such as CCl_4 or CaC_2 even at 600 to 700°C.

LOWER CARBIDES

Most preparative methods describe the synthesis of carbides of the limiting composition NbC and TaC. However, method I (or, if properly executed, also the above-described crystal growing procedure) also gives products with a low C content, e.g., products corresponding to the lower carbides Nb_2C (and Ta_2C).

PROPERTIES:

Iron-gray to dark-gray powders; the sintered solid exhibits a bright metallic luster; tarnishing frequently changes the surface color to brown to yellow. Does not lose carbon at high temperatures in the presence of hydrogen, provided a small amount of hydrocarbons is present in the gas (see method IIb). Stable to N_2 up to about 3300°C. Quite sensitive to O_2 and H_2O on heating, undergoing rapid oxidation above 800°C in air. Not very volatile in high vacuum up to 3000°C.

NbC: m.p. 3500°C; d 7.6.

TaC: m.p. 3900°C; d 13.9.

REFERENCE:

Ia. C. Agte and K. Moers. Z. anorg. allg. Chem. 198, 233 (1931); G. Brauer, H. Renner and J. Wernet. Z. anorg. allg. Chem. 277, 249 (1954); G. Brauer and R. Lesser. Z. Metallkunde 49, 622 (1958); 50, 8 (1959); E. K. Storms and N. H. Krikorian, J. Phys. Chem. 63, 1747 (1959); R. P. Elliott. A.S.M. Preprint No. 179 (1960).

Ia, b. K. Becker and H. Dwes. Z. techn. Physik 11, 148 (1930).

II. E. Friederich and L. Sittig. Z. anorg. allg. Chem. 144, 169 (1925); C. Agte and K. Moers. Z. anorg. allg. Chem. 198, 233 (1931); A. Y. Kovalskiy and Y. S. Umanskiy. Zh. Fizich. Khimii 20, 769 (1946); Chem. Zentr. 47, II, 1546.

SECTION 24

Chromium, Molybdenum, Tungsten, Uranium

F. HEIN and S. HERZOG

Chromium

Cr

I. $$\underset{152.0}{Cr_2O_3} + \underset{53.9}{2\,Al} = \underset{104.0}{2\,Cr} + \underset{101.9}{Al_2O_3}$$

An intimate mixture of 70 g. of pure ignited Cr_2O_3, 33 g. of Al granules (or Al powder), and 25 g. of fused and powdered $K_2Cr_2O_7$ is placed in a clay crucible whose bottom is covered with 10 g. of CaF_2. The mixture is caused to react by means of ignition mixture and a strip of Mg.* After cooling, the contents of the crucible are broken up, and the spheres of metal are mechanically extracted. This gives about 99% pure chromium metal in 50–75% yield (the larger the quantity of reactants, the better the yield).

II. $$\underset{651.0}{2\,K_2[CrCl_5(H_2O)]} + \underset{37.0}{3\,Mg} = \underset{104.0}{2\,Cr} + 3\,MgCl_2 + 4\,KCl + 2\,H_2O$$

The $K_2[CrCl_5(H_2O)]$ is obtained by dissolving 100 g. of $K_2Cr_2O_7$ in the minimum quantity of water, treating the solution with 400 ml. of HCl (d 1.124), and gradually adding 100 ml. of 80% alcohol. The reaction is accompanied by vigorous evolution of heat. Then, 170 g. of KCl is added and completely dissolved, the mixture filtered, and the filtrate evaporated to dryness. The mass is then completely dehydrated by further heating. The resulting violet solid is then

*The ignition mixture, called "Zündgemisch" or "Zündkirsche" (igniting cherry), consists of an intimate mixture of 15 parts by weight of barium peroxide and 2 parts of powdered magnesium metal held together with collodion. The whole is wrapped in magnesium ribbon, which acts as fuse (H. Blücher, Auskunftsbuch für die chemische Industrie [Data Book for the Chemical Industry], 18th ed., de Gruyter, Berlin, 1954, p. 1314).

ground, and any green portions are removed as completely as possible. The potassium chromium (III) chloride thus obtained is mixed with 50 g. of Mg filings. The mixture is placed in a covered Hessian crucible, brought to red heat and held at this temperature for one half hour. However, not all of the KCl must be allowed to volatilize, otherwise a fraction of the Cr will be converted to the oxide and will contaminate the product. After this calcination, the crucible is cooled and broken. The shards and the particles of green chromium oxide, which appear on the surface of the gray-black melt, are removed. The mechanically cleaned mass is then placed in water, where it crumbles to a powder. The soluble salts are removed by decantation. The residue is boiled with dilute nitric acid to remove the excess Mg (and the MgO which has formed from it).

Any $Mg(NO_3)_2$ and excess acid present are separated by further decantation; filtration is not recommended because of the fine particle size of the metal. The Cr residue is dried on a steam bath. Yield about 27 g. of light-gray, microcrystalline powder whose Cr content is 99.6%.

III. ELECTROLYSIS

The electrolytic cell consists of a beaker with a copper cathode rod suspended in the center. A lead sheet or a coil of lead tubing placed along the wall of the cell serves as the anode; if the latter arrangement is used, cold water is circulated through the tubing. The electrolyte consists of a solution of 240 g. of CrO_3, 3 g. of $Cr_2(SO_4)_3 \cdot 12\ H_2O$, and 8.8 g. of $Cr(OH)_3 \cdot 3\ H_2O$ in one liter of water. A current density of 0.10 amp./cm.^{2} and a potential of 3.2 volts are used. It is essential that the electrolyte remain undisturbed (no stirring) during electrolysis. The thick layer of Cr which forms on the cathode in a few days is readily stripped off. If it should prove necessary to remove the H_2 which accumulates in the metal voids during deposition of the Cr, the product should be heated to 600°C in high vacuum.

IV. Ductile Cr is obtained from $CrCl_3$ and Ca in a steel bomb under argon. For details of the method, see section on Titanium, p. 1161.

PROPERTIES:

Atomic weight 52.01. Solid Cr has a silvery luster; very hard and brittle, but very pure Cr is ductile. M.p. about 1920°C (in vacuum), b.p. about 2200°C; d^{25} 7.138. Body-centered cubic crystals; hexagonal form also exists.

REFERENCES:

I. G. Jander, Lehrbuch für das anorg. chem. Praktikum [Textbook of Inorg. Chem. Practice], 5th ed., 1944, p. 188.
II. H. Funk, Darst. der Metalle im Laboratorium [Preparation of Metals in the Laboratory], Stuttgart, 1938, p. 66.
III. Private communication from Prof. G. Grube. See H. Haraldsen and E. Kowalsky. Z. anorg. allg. Chem. 224, 330 (1935).
IV. W. Kroll. Z. anorg. allg. Chem. 226, 23 (1935).

Chromium (II) Chloride

$CrCl_2$

I. $$\underset{158.4}{CrCl_3} + \underset{11.2\ l.}{{}^1/_2 H_2} = \underset{122.9}{CrCl_2} + HCl$$

The special vessel (2.5 × 50 cm., Fig. 313) used for the reduction is made of high-melting glass. For reasons of safety it is first baked in vacuum at 500°C while empty. It is provided with a two-hole rubber stopper, through which the outlet tube *a* and the longer inlet tube *b* (8-mm. diameter) are inserted. The reactor is charged with $CrCl_3$ (prepurified by sublimation in a stream of Cl_2). The tube is heated to 500°C in a thermostatically controlled electric

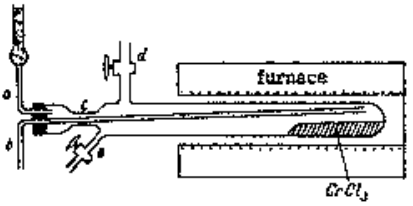

Fig. 313. Preparation of chromium (II) chloride. *b* inlet tube for hydrogen, H_2-HCl mixture, or nitrogen; *d* stopcock with 10-mm. bore for withdrawal of reaction product.

furnace, while a mixture of H_2 and HCl (the latter serving to hinder any further reduction to Cr) is admitted through *b* (the dry, O_2-free, 50 ml./min. gas streams are mixed in a tee prior to introduction into the apparatus). The outlet tube *a* is connected to a drying tube filled with $CaCl_2$. To test for completeness of reduction, the furnace is removed briefly from time to time (pure $CrCl_2$ is white). When

the reaction is complete, the furnace is cooled, the H_2–HCl mixture displaced with dry N_2 or CO_2, and the inlet tube pulled back until its tip is at the rubber stopper. The reactor tube is then melt-sealed at constriction *c*. Any required quantity of $CrCl_2$ can be shaken out of the tube through the 10-mm.-bore stopcock *d*; in this operation, the $CrCl_2$ must always be under dry, O_2-free inert gas, which is admitted through stopcock *e*. (For special apparatus for storage under inert gas, see also Part I, pp. 71 and 75.)

II. $$\underset{52.0}{Cr} + 2\,HCl = \underset{44.8\,l.}{CrCl_2} + \underset{122.9}{H_2}$$

A small porcelain boat is charged with pea-sized pieces (or, better, powder) of metallic Cr and inserted in a quartz reactor tube. Dry, O_2-free HCl is passed through the tube, which is heated to as high a temperature as possible (1150 to 1200°C). On cooling in the HCl stream, an asbestoslike mass of white (or, if impure, gray) crystalline needles of $CrCl_2$ is obtained. Because of its toughness, the mass is very difficult to remove from the boat. The preparation must be sealed as rapidly as possible into a sample tube filled with N_2 or CO_2; if this is not done, the anhydrous $CrCl_2$ is rapidly hydrated by atmospheric moisture, after which oxidation also occurs at once. Because of its high melting point, some metal may be trapped within the chloride and thus remain unreacted.

III. $$\underset{340.2}{Cr_2(CH_3COO)_4} + \underset{145.8}{4\,HCl} \xrightarrow{\text{ether}} \underset{245.9}{2\,CrCl_2} + 4\,CH_3COOH$$

Ten grams of fine chromium (II) acetate hydrate $Cr_2(CH_3COO)_4 \cdot 2\,H_2O$ crystals is dehydrated in a three-neck flask at 110 to 120°C (aspirator vacuum); the color changes from brick-red to brown. Then, 60 ml. of air-free ether is added and dry HCl is passed through the vessel with the suspension (the vessel is in an ice bath and is protected against atmospheric moisture by a P_2O_5 tube). After several minutes, a violet color is observed in the solution, and the chromium acetate powder is transformed (with an increase in bulk) into chromium (II) chloride which still contains some acetic acid. The flask is swirled during this operation to prevent clogging of the inlet tube. The white crystals are filtered in the absence of air, washed with absolute, air-free ether, and dried at 110 to 120°C. The acetic acid is thus eliminated, and pure white, analytically pure $CrCl_2$ is obtained as a residue. Yield 4–5 g.

PROPERTIES:

White crystals or fused, fibrous mass. M.p. 824°C; d_4^{14} 2.751. Very hygroscopic. Can be sublimed in vacuum. Dissolves readily in water, giving a sky-blue solution.

REFERENCES:

I. J. Reschke. Thesis, Univ. of Leipzig, 1925, p. 43; F. Hein. Z. anorg. allg. Chem. 201, 314 (1931); F. Ephraim. Helv. Chim. Acta 17, 291 (1934); A. B. Burg in: L. F. Audrieth. Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 150.
II. J. Koppel. Z. anorg. Chem. 45, 361 (1905); W. Biltz and E. Birk. Z. anorg. allg. Chem. 134, 134 (1924); W. Fischer. Z. anorg. allg. Chem. 222, 309 (1935); H. Hecht. Präparative Anorganische Chemie [Preparative Inorganic Chemistry], Berlin-Göttingen-Heidelberg, 1951, p. 80.
III. Private communication from F. Hein, E. Kurras and W. Kleinwächter (unpublished).

Chromium (III) Chloride

$CrCl_3$

I. $$\underset{104.0}{2\,Cr} + \underset{66.0\ L.}{3\,Cl_2} = \underset{316.8}{2\,CrCl_3}$$

Coarse Cr metal powder (10–20 g.) is placed in a 50-cm.-long and 3-cm.-I.D. horizontal porcelain reactor tube, which is heated in a blast lamp flame. It is essential that all residual air be displaced by a fast stream of completely dry Cl_2 (for at least half an hour prior to introduction of the Cr). The temperature is then raised as high as possible; the tube is allowed to cool, and the Cl_2 is displaced with dry CO_2. Violet leaflets of $CrCl_3$ form, with a large increase in volume (to avoid plugging the tube as a result of this volume increase, the Cr reactant should be distributed over a long stretch of the tube).

The $CrCl_3$ is purified by sublimation in the stream of Cl_2, then repeatedly boiled with conc. HCl, washed with distilled water until disappearance of chloride reaction, and dried at 200 to 250°C.

The high sublimation temperature of over 1200°C is a disadvantage of this method. Under certain conditions the procelain tube can be markedly corroded in this operation and, in addition, it may be plugged as a result of the large volume increase occurring during the formation of the chromium (III) chloride. The following method, in which green chromium (III) chloride hydrate is dehydrated in a stream of CCl_4 at 500°C, avoids these difficulties.

II. OVERALL EQUATION:

$$[CrCl_2(OH_2)_4]Cl \cdot 2\,H_2O = CrCl_3 + 6\,H_2O$$

SIDE AND INTERMEDIATE REACTIONS:

$$2[CrCl_2(OH_2)_4]Cl \cdot 2\,H_2O = Cr_2O_3 + 6\,HCl + 9\,H_2O$$

$$Cr_2O_3 + 3\,CCl_4 = 2\,CrCl_3 + 3\,COCl_2$$

$$2\,Cr_2O_3 + CCl_4 = 4\,CrCl_3 + CO_2$$

Thus, one by-product is phosgene, which must be carefully vented (use a hood!). Simple absorption in water is not adequate, since the hydrolysis is not instantaneous.

The apparatus is shown in Fig. 314. Forty grams of green chromic chloride is placed in quartz flask *c*, which is placed in an electric furnace capable of delivering 650°C. The apparatus for generating and superheating CCl_4 vapor is then attached. This apparatus consists of the 250-ml. distilling flask *a* with its superposed dropping funnel and a U tube immersed in a silicone oil bath at 150°C.

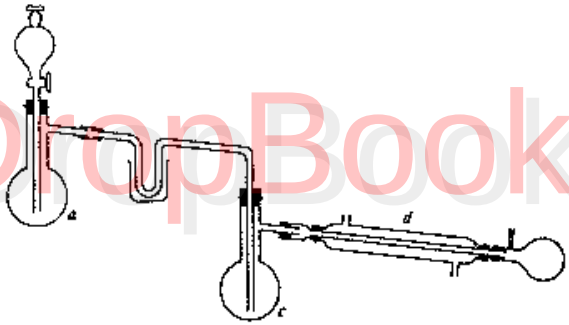

Fig. 314. Dehydration of chromium (III) chloride hydrate with carbon tetrachloride.

After brief heating of the furnace (flask temperature of 100–150°C), one drop of CCl_4 per second is admitted from the dropping funnel into flask *a*, which is heated with a Bunsen burner in such a manner that each drop vaporizes at once. After some time (furnace temperature of about 300°C), a mixture of water, CCl_4, etc., distills over. It condenses in *d*; the noncondensing gases (including phosgene) are vented through the hood. After some two hours of reaction, when the furnace temperature has reached 650°C, the gas stream is interrupted and the apparatus allowed to cool. The anhydrous $CrCl_3$ remains in the flask in about 90% yield (some of it sublimes). The lustrous violet crystalline leaflets are extracted with boiling dilute HCl and dried. About 20 g. of chromium (III) chloride is obtained.

PROPERTIES:

Formula weight 158.38. Red-violet crystalline scales with metallic luster. M.p. ~ 1150°C. May be sublimed in Cl_2 stream; rate of solution in water, acids and organic solvents immeasurably slow. Addition of a very small amount of $CrCl_2$ aids in rapid solution of $CrCl_3$ in water or alcohol.

REFERENCES:

I. Private communication from H. Hecht, Greifswald; F. Hein, Z. anorg. allg. Chem. 201, 314 (1931).
II. G. B. Heisig, B. Fawkes and R. Hedin in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 193; A. Vavoulis et al. Ibid., Vol. VI, New York-London, 1960, p. 129.

Chromium (II) Bromide

$CrBr_2$

I. $$\underset{291.8}{CrBr_3} + \underset{11.2\,l.}{0.5\,H_2} = \underset{211.8}{CrBr_2} + HBr$$

A weighed quantity of $CrBr_3$ is reduced to constant weight in a U tube at 350–400°C for 6–10 hours. The most painstaking purification of the H_2 is essential for success. For uniform heating, the U tube is surrounded with an asbestos box.

II. $$\underset{340.2}{Cr_2(CH_3COO)_4} + \underset{323.7}{4\,HBr} \xrightarrow{\text{ether}} \underset{423.7}{2\,CrBr_2} + 4\,CH_3COOH$$

The procedure is the same as for chromium (II) chloride (method III), but hydrogen bromide is used instead of hydrogen chloride.

PROPERTIES:

White crystalline powder; d_2^{25} 4.356. Soluble in air-free water, yielding a blue color. Rapidly oxidized in air.

REFERENCES:

I. W. Biltz and E. Birk, Z. anorg. allg. Chem. 134, 134 (1924); W. Fischer and R. Gewehr, Ibid. 222, 309 (1935).
II. Private communication from F. Hein, E. Kurras and W. Kleinwächter (unpublished).

Chromium (III) Bromide

$CrBr_3$

$$\underset{104.0}{2\,Cr} + \underset{479.5}{3\,Br_2} = \underset{583.5}{2\,CrBr_3}$$

Electrolytic Cr powder is spread in a thin layer in a quartz reactor tube and bromine vapor, predried over P_2O_5, is passed over the Cr in a stream of O_2-free, dry N_2 or Ar. The quartz tube is heated to about 1000°C, whereupon the two elements combine with incandescence at the beginning of the reaction. The unconverted Br_2 is condensed in a receiver cooled in ice-salt mixture. After 45-60 minutes, the material is allowed to cool while maintaining the gas stream. The lustrous black, leafy crystals of $CrBr_3$ are purified by several extractions with absolute ether and decantations with ice water (to remove traces of adhering $CrBr_2$). This is followed by washing with absolute alcohol and ether; the product is dried in a vacuum desiccator over P_2O_5.

PROPERTIES:

Formula weight 291.76. Black lustrous crystals, green in transmitted and reddish in reflected light. Soluble in water only upon addition of Cr (II) salts.

DropBooks

REFERENCES:

J. Reschke. Thesis, Univ. of Leipzig, 1925; F. Hein and I. Wintner-Hölder. Z. anorg. allg. Chem. 201, 319 (1931).

Chromium (II) Iodide

CrI_2

$$\underset{52.0}{Cr} + \underset{259.8}{I_2} = \underset{305.9}{CrI_2}$$

The starting materials are electrolytic Cr reduced to the size of millet seed and I_2 resublimed over KI (see p. 277). The apparatus is shown in Fig. 315. The quartz reactor tube a has an overall length of about 56 cm. and an I.D. of 2 cm. (2.5 cm. at the bulged-out section). The tube ends (on the right side of the drawing) in a quartz capillary spiral which is somewhat constricted at c; on the opposite side, it can be closed off by a large-diameter ground joint connected to stopcock h_1. The cooling trap b is

connected via stopcock h_2 to a tee adapter; thus, it can be in line either with the high-vacuum system (via stopcock h_3) or with the two-way stopcock z, which in turn leads either to the N_2 source or to a vacuum oil pump.

The movable tubular resistance furnace o serves to heat the quartz reactor at any desired spot.

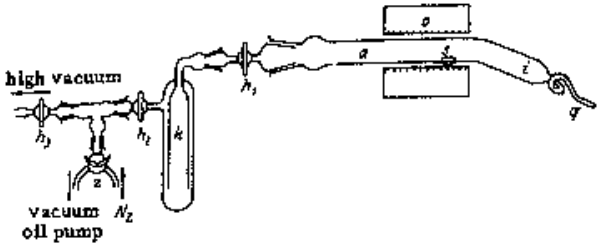

Fig. 315. Preparation of chromium (II) iodide. a quartz reactor tube; s boat with Cr; o electric furnace; k cold trap.

First, a trace of very fine Cr powder is placed in the tip of the capillary spiral, and then I_2 (10% excess over the stoichiometric quantity) is placed in the slightly inclined tube section i. A small porcelain boat with the Cr is placed in the bulge s. Trap k is now cooled to −80°C and the apparatus is evacuated (with stopcock z closed) to < 0.001 mm.

The vacuum is then broken with N_2 and the evacuation repeated (this procedure is repeated 3 or 4 times). Stopcock h_1 is closed and the Cr powder at the tip of the spiral is heated with a torch to a bright red glow to bind the last traces of O_2. Then the tube furnace is set in place over spot s and the Cr heated at 700 to 850°C; to minimize undesirable heat losses, asbestos paper (not shown in the figure) is placed in both furnace openings. As the I_2 now diffuses slowly toward the Cr, the nascent CrI_2 solidifies as a crystalline mass at both sides of the tube protruding from the furnace. This slow procedure yields very beautiful leaf- or needle-shaped red-brown to iodine-colored crystals. At the beginning of the iodination, a deep-black coating always forms on the colder portions of the tube; this material is more volatile than CrI_2 and converts to CrI_2 at higher temperatures, evolving iodine. Even though the CrI_3 itself is not particularly volatile, the crystal deposit extends on both sides for up to 2 cm. beyond the hot zone. By gradually shifting the furnace, the crystalline deposit is shifted away from the spot where the Cr is situated; in this way, one prevents it from becoming too dense and provides a surface for fresh deposition. By following this procedure, almost all the I_2 is introduced little by little, with the long heating producing a type of resublimation

and yielding beautiful single crystals. Such a run takes 8–14 days; some unreacted metal is still invariably found after this time at the bottom of the boat, because the sublimation of CrI_2 from the (protective) melt is very slow. When the iodination has proceeded as far as possible, the excess I_2 must be displaced before the CrI_2 itself can be removed. Thus, the reactor is connected to the high vacuum (via h_3), with the cold trap at −80°C. The I_2 is driven off by careful fanning with a flame (250–300°C) and continuous evacuation. Evacuation is continued after complete removal of the I_2 until the quartz tube is cool; the apparatus is then closed off at h_1.

Transfer of the CrI_2 from the reactor requires great care, since the compound is extremely sensitive to air and moisture. Further, the solid material possesses a relatively large surface. The following procedure is the safest: The vacuum is broken with compressed N_2 via h_1, and pressure above atmospheric is created in the apparatus. The quartz capillary is then broken off at q and this opening is attached to another N_2 connection. The

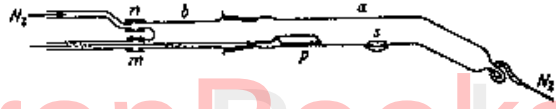

Fig. 316. Transfer of chromium (II) iodide following its preparation. *a* reaction tube of Fig. 315; *p* porcelain boat with front wall broken off (scoop).

joint with h_1 is then removed and the adapter tube *b* is inserted in its place, as shown in Fig. 316 (an N_2 stream also passes through *b*). The adapter carries at one end the same standard taper joint as h_1, and at the other end two short connectors *m* and *n*. An N_2 stream enters at *n*; a long glass rod, the forward end of which is bent into a small hook, is introduced through *m*. This hook supports a fairly large porcelain boat *p*, whose front wall is broken off at a sharp angle. The boat is of such a size that it is still able to move in the quartz reactor. Now, with the fast N_2 stream always maintained, this "dredge" is pushed forward through the loose crystal aggregate, whereupon most of the latter drops into boat *s*. This operation is aided by gentle tilting and tapping of the reactor. The filled boat *s* is now pulled back into the adapter *b*; the adapter is quickly detached from the reactor and closed off with a ground cap. Finally the boat with the CrI_2 is transferred for storage into a tube provided with a ground joint (see Part I, p. 75); as a precaution, this tube is evacuated several times and then filled with N_2 (slight gage pressure). All of these operations must be carried out in sequence and without undue delay.

PROPERTIES:

Brown-red leaflets; thin leaflets are somewhat transparent, thick crusts often have an iodinelike color. Very sensitive to air and moisture, easily soluble, with bright blue color, in air-free water. M.p. 790-795°C; d_4^{20} 5.02$_3$.

REFERENCE:

F. Hein and G. Bähr. Z. anorg. allg. Chem. 251, 241 (1943).

Chromium (III) Iodide

CrI_3

$$\underset{104.0}{2\,Cr} + \underset{761.5}{3\,I_2} = \underset{865.5}{2\,CrI_3}$$

The apparatus (Fig. 317) is made of high-melting glass. The diameter of the tube at *e*, *f* and *h* is 25-30 mm. Three grams of fine chromium metal powder (electrolytic chromium is best) is introduced into *e*, and an excess (30 g.) of iodine into *h*. Then *k* is sealed off and the apparatus is evacuated to appr. 10^{-5} mm. (with occasional gentle heating). The iodine is now sublimed into *f* by cooling the latter section (Dry Ice) and heating *h* (during this operation stopcock *b* is turned off and on). Following this, *g* is sealed off in high vacuum, and then *d* is sealed off as well.

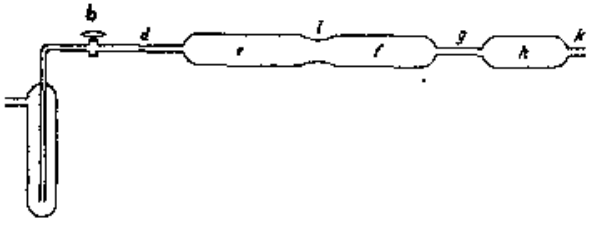

Fig. 317. Apparatus for synthesis of chromium (III) iodide.

Now sections *e* and *f* are enclosed in separate tubular furnaces; *e* is heated for 24 hours at 475°C, and *f* for the same period at 225°C. (The vapor pressure of iodine at this temperature is approximately 3 atm.) The apparatus is then allowed to cool, and the unreacted iodine is sublimed out from *e* (which is held at 100°C) into *f* (held at room temperature). The tube is then broken, in dry

air, at constriction 1 (careful!). The material is transferred to a suitable storage vessel, which is then evacuated for some time to remove the last traces of iodine. The yield is almost quantitative.

If necessary, further purification may be achieved by heating for several hours at 500°C in an evacuated quartz tube. This operation yields chromium (II) iodide; the iodide can be sublimed in vacuum at 700°C and finally reiodinated as described above.

PROPERTIES:

Black crystals; dissolve rapidly in water upon addition of some Cr (II) iodide. Stable at room temperature; thermally dissociated at higher temperatures according to: $2\ CrI_3 = 2\ CrI_2 + I_2$. The iodine pressure reaches 1 atm. at about 670°C.

REFERENCES:

L. L. Handy and N. W. Gregory. J. Amer. Chem. Soc. 72, 5049 (1950); N. W. Gregory and L. L. Handy in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 128.

Chromium (III) Hydroxide

$Cr(OH)_3 \cdot n\,H_2O$

DropBooks

I. A-HYDROXIDE $Cr(OH)_3 \cdot 3\,H_2O$

A solution of 12 g. of gray-blue $[Cr(H_2O)_6]Cl_3$ (for preparation, see p. 1348 f.) in 500 ml. of water is treated with 100 ml. of 2 N ammonia. After settling of the precipitate (centrifuge if necessary), the mother liquor is decanted; the suspension is filtered through a leaf filter, thoroughly washed until free of NH_4Cl, and dried in air.

PROPERTIES:

Bright blue-green powder; gives blue salts of the $[Cr(H_2O)_6]X_3$ type with dilute acids.

B-HYDROXIDE $Cr(OH)_3 \cdot 3\,H_2O$

The procedure for the preparation of the A-hydroxide is followed, but one starts with 12 g. green of $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$.

PROPERTIES:

Dark blue-green powder; gives green salts of the $[Cr(H_2O)_4X_2]X \cdot 2\,H_2O$ type with dilute acids. In contrast to the A-type, the B-hydroxide is insoluble in acetic acid.

II. $$2\,CrO_3 + 3\,C_2H_5OH = 2\,Cr(OH)_3 + 3\,CH_3CHO + 3\,H_2O$$
$$(-n\,H_2O)$$

This is a convenient method for preparation of larger quantities of $Cr(OH)_3$. A solution of 160 g. of CrO_3 in 2 liters of water is prepared and alcohol (8 portions of 10 ml. at 5-minute intervals) is added with vigorous stirring (caution: a hood is needed!). After 4 hours of standing, an additional 80 ml. of alcohol is added in the same manner. The mixture is then refluxed for 16 hours (stirring is required to avoid bumping). The finely divided, dark brown precipitate is filtered through a 24-cm.-diameter Büchner funnel and dried at 110°C without washing. Yield: 145 to 150 g. Additional quantities (30-35 g.) can be recovered from the filtrate by concentration of the latter. Alternately, the Cr-containing liquid may be used as solvent (instead of water) in the next run.

PROPERTIES:

This method affords a black product with a pitchlike luster, probably because of a small admixture of higher oxides. This material has a higher catalytic activity than that obtained by precipitation.

REFERENCES:

I. A. Hantzsch and E. Torke. Z. anorg. allg. Chem. 209, 73 (1932).
II. R. F. Ruthruff in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 190.

Chromium Sulfides

CrS, Cr_2S_3

I.
$$\underset{52.0}{Cr} + \underset{32.1}{S} = \underset{84.1}{CrS}$$
$$\underset{104.0}{2\,Cr} + \underset{96.2}{3\,S} = \underset{200.2}{Cr_2S_3}$$

The sulfides are prepared by heating exact stoichiometric mixtures of electrolytic Cr (for preparation, see p. 1335) and pure S for 24 hours in small, evacuated, sealed quartz tubes placed in an electric furnace at 1000°C. All of the S does not react even if heated for 3-4 days and slowly cooled. The product is freed of unreacted sulfur by fanning with a Bunsen flame while simultaneously cooling the empty seal-off point of the tube. The

quantity of S which condenses in that section is determined by reweighing, and the composition of the sulfide is calculated by using this value.

Cracking of the quartz tube during cooling of preparations which are high in S can be avoided by sealing the reaction vessel proper in a second, similarly evacuated quartz tube.

II. $$2\,CrCl_3 + 3\,H_2S = Cr_2S_3 + 6\,HCl$$
316.8 67.4 l. 200.2

Exactly stoichiometric Cr_2S_3 may be obtained by heating $CrCl_3$ in a stream of H_2S at 600–650°C.

PROPERTIES:

The chromium sulfide preparations obtained via method I have a metallic appearance and become fused at the temperature of preparation. The CrS possesses a hexagonal superstructure of the B 8 type, while at 59.7 atom% of S, a B 8 structure with the axial ratio $c/a = 1.62_5$ has been shown to exist. The Cr_2S_3 obtained by method II consists of hexagonal black leaflets, resistant to non-oxidizing acids, easily soluble in HNO_3.

DropBooks

REFERENCES:

I. H. Haraldsen and E. Kowalsky. Z. anorg. allg. Chem. 224, 331 (1935); H. Haraldsen and A. Neuber. Ibid. 234, 338 (1937).
II. W. Rüdorff and E. Stegemann. Z. anorg. allg. Chem. 251, 390 (1943).

Chromium Nitride

CrN

I. $$Cr + \tfrac{1}{2}N_2 = CrN$$
52.0 11.4 l. 66.0

Electrolytic chromium powder is heated for 2 hours at 800–900°C in a quartz or porcelain tube while a dry, O_2-free stream of N_2 is passed through. After cooling, the product is ground in an agate mortar and calcined again for 2 hours in a stream of N_2. The final product is treated with HCl until nothing further dissolves (the HCl liquid remains colorless). The black residue is thoroughly washed and dried.

II. $$\underset{158.4}{CrCl_3} + 4\,NH_3 = \underset{66.0}{CrN} + 3\,NH_4Cl$$
$$\underset{88.31.}{}$$

A tube of high-melting glass (25–30 cm. long) is used and 5–10 g. of anhydrous $CrCl_3$ is calcined, first gently and then vigorously, in a stream of NH_3. The heat source is a series of burners. The NH_3 is obtained either from a bomb or by heating about 300 ml. of conc. ammonia; it is dried by passage through a lime tower and a large U tube filled with CaO. The reactor tube carries no outlet tube, since the latter would be plugged by sublimed NH_4Cl (use a hood!). Strong heating is continued until no further NH_4Cl vapor is evolved; then (after cooling) the product is ground and recalcined in a stream of NH_3. The yield is almost quantitative.

If it is desired to remove traces of $CrCl_3$, the product is extracted in the cold with some dilute HCl (add some Sn), then washed with water, filtered and dried at 100–120°C.

PROPERTIES:

Black, magnetic powder; insoluble in acids and alkalies; d 5.9. Crystal structure: NaCl type.

REFERENCES:

I. F. Briegleb and A. Geuther. Liebigs Ann. 123, 239 (1862); R. Blix. Z. phys. Chem. B 3, 236 (1929).
II. H. Biltz and W. Biltz. Übungsbeispiele aus der unorg. Experimentalchemie [Exercises in Experimental Inorganic Chemistry], 3rd and 4th eds., 1920, p. 20.

Hexaaquochromium (III) Chloride

$$[Cr(OH_2)_6]Cl_3$$

I. $$\underset{(\cdot 3\,H_2O)\ 400.2}{[Cr(OH_2)_6](NO_3)_3} + 3\,HCl = \underset{266.5}{[Cr(OH_2)_6]Cl_3} + 3\,HNO_3$$

A solution of 100 g. of chromium (III) nitrate $Cr(NO_3)_3 \cdot 9\,H_2O$ in 100 ml. of H_2O and 100 ml. of 38% HCl is prepared. Hydrogen chloride gas, predried in H_2SO_4, is introduced with ice cooling, until the precipitation of $[Cr(H_2O)_6]Cl_3$ is complete.

The crystal slurry is rapidly filtered on a large glass suction funnel and washed with some fuming HCl. It is dissolved in 100 ml. of water and 100 ml. of fuming HCl, and reprecipitated with HCl gas while cooling in ice. After precipitation is complete, the

greenish supernatant solution is decanted and the gray-blue chloride is freed of most of the adhering HCl and the green chloride by stirring three times with acetone. The remaining impurities are completely extracted by treating the product with small quantities of acetone on a fritted-glass funnel (the filtrate must become colorless in the end). The acetone is removed by rinsing with absolute ether. The salt is freed of ether and traces of moisture by drying in a desiccator over H_2SO_4. The yield is about 72%.

II. $$\underset{266.5}{[CrCl_2(H_2O)_4]Cl \cdot 2H_2O} = \underset{266.5}{[Cr(H_2O)_6]Cl_3}$$

A solution of 50 g. of green chromium chloride hydrate in 50 g. of water is refluxed for one half hour, during which time almost no color change is observed. The flask is then cooled by immersion in an ice-salt mixture and HCl gas is introduced with periodic shaking of the flask. The temperature inside the flask must always be held below 0°C; this is achieved by frequent renewal of the freezing mixture. After saturation with HCl, the fine powder which separates is allowed to settle to the bottom and the supernatant blue-green liquid is decanted. The powder itself is rinsed out of the flask onto a fritted glass funnel with cold saturated HCl, dried as much as possible by suction, then stirred with acetone and washed until the acetone is no longer green. As soon as the acetone traces have evaporated, the crude product is dissolved in 20 ml. of water; it is filtered if necessary, and HCl gas is introduced into the blue solution (while cooling the flask with cold water) until saturation. At this point the gas flow is interrupted and the flask is placed in finely crushed ice. The solution becomes almost colorless after some time while the chloride separates in granular, blue-gray crystals. After filtering through a fritted-glass funnel, the product is washed with acetone and dried over H_2SO_4. Yield: 12 g.

III. $$KCr(SO_4)_2 \cdot 12H_2O + 3HCl \rightarrow [Cr(H_2O)_6]Cl_3$$

Chrome alum (250 g.) is dissolved in a chilled mixture of 1 liter of conc. hydrochloric acid and 250 ml. of water. The solution is filtered and saturated with hydrogen chloride gas at 10 to 15°C. It becomes almost colorless during this step, and the crude product separates in crystalline form. The crystals are filtered and purified by dissolving in 175 ml. of water, reprecipitating at 10°C as described above, filtering again, washing with dry acetone, and drying over sulfuric acid. Yield: about 90 g.

PROPERTIES:

Blue-gray crystals, very deliquescent in air, soluble in water with a blue-violet color, readily soluble in alcohol, insoluble in acetone.

DropBooks

REFERENCES:

I. A. Hantzsch and E. Torke. Z. anorg. allg. Chem. 209, 72 (1932).
II. A. Werner and A. Gubser. Ber. dtsch. chem. Ges. 34, 1591 (1901).
III. G. O. Higley. J. Amer. Chem. Soc. 26, 620 (1904).

Chloropentaaquochromium (III) Chloride

$$[CrCl(OH_2)_5]Cl_2 \cdot H_2O$$

A) $$\underset{(\cdot 2\,H_2O)\ 266.5}{[CrCl_2(OH_2)_4]Cl} + \underset{98.1}{H_2SO_4} = \underset{(\cdot 3\,H_2O)\ 327.7}{[CrCl(OH_2)_5]SO_4} + 2\,HCl$$

B) $$\underset{(\cdot 3\,H_2O)\ 327.7}{[CrCl(OH_2)_5]SO_4} + 2\,HCl = \underset{(\cdot H_2O)\ 266.5}{[CrCl(OH_2)_5]Cl_2} + H_2SO_4$$

A) PREPARATION OF $[CrCl(OH_2)_5]SO_4 \cdot 3\,H_2O$

A solution of 26.8 g. of green chromium chloride hydrate $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$ in an equal amount of water is allowed to stand for 24 hours at room temperature, and a mixture of 10 g. of conc. H_2SO_4 and 4 g. of water is then added. The sulfate soon separates in bright green tablets.

B) PREPARATION OF $[CrCl(OH_2)_5]Cl_2 \cdot H_2O$

A conc. aqueous solution of the sulfate, cooled to 0°C, is allowed to flow into ether at 0° while a stream of dry HCl is introduced. The yield is greater than 87%.

PROPERTIES:

Bright green, microcrystalline, very hygroscopic powder; readily soluble in water, alcohol and acetone. Differentiated from its isomers by its solubility in a mixture of equal volumes of ether and fuming hydrochloric acid. Insoluble in HCl-saturated ether.

REFERENCES:

I. R. F. Weinland and Th. Schumann. Ber. dtsch. chem. Ges. 40, 3094 (1907).
II. M. Gutiérrez de Celis. An. Soc. Españ. Fisica Quim. 34, 553 (1936), abstract in Chem. Zentr. 1936, II, 1874.

Hexaamminechromium (III) Chloride and Nitrate

$[Cr(NH_3)_6]Cl_3$, $[Cr(NH_3)_6](NO_3)_3$

I. PREPARATION BY AUTOOXIDATION OF AN NH_4Cl-CONTAINING AMMONIACAL SOLUTION OF A Cr(II) SALT

A solution of chromium (II) salt is prepared as indicated in the preparation of rhodochromium chloride (see p. 1359). This solution is forced under pressure (in the absence of air) into a flask containing a mixture of 525 g. of NH_4Cl and 540 g. of ammonia (d 0.91). The vessel should be almost full at this point. The flask is stoppered at once with a cork which carries a gas outlet tube; the tube terminates under water. The flask is placed in cold water until H_2 evolution ceases (about 18–24 hours). The $[Cr(NH_3)_6]Cl_3$ that deposits on the undissolved NH_4Cl and that dissolved in the liquid are worked up separately.

The red solution is decanted and treated with an equal volume of 95% alcohol. The chloride, which settles after several hours, is washed by decantation with alcohol, filtered, rewashed with alcohol, and dried in air. It is then dissolved in lukewarm water and the solution passed through a filter into well-cooled nitric acid (d 1.39), whereupon the $[Cr(NH_3)_6](NO_3)_3$ separates in long, yellow needles. The precipitate is washed several times by decantation with nitric acid, then with a mixture of 1 volume of nitric acid and 2 volumes of water, filtered, washed with alcohol until free of the acid, and dried in the air.

The product-containing NH_4Cl is treated several times with 150-ml. portions of water at room temperature, but only as long as the extracts are still yellow. They are treated with an equal volume of nitric acid (d 1.39; good cooling is essential). Yellow needles appear, either at once or after several hours; they are worked up as above. Total yield: 35–40 g.

The salt is purified by dissolving in a minimum quantity of cold water. The solution is passed through a filter into dilute nitric acid (1 vol. of nitric acid, d 1.4, and 2 vol. of water); the crystals are washed with alcohol and dried in air.

II.

$$\underset{158.4}{CrCl_3} + 6\,\underset{102.2}{NH_3} = \underset{260.6}{[Cr(NH_3)_6]Cl_3}$$

$$\underset{260.6}{[Cr(NH_3)_6]Cl_3} + 3\,\underset{189.0}{HNO_3} = \underset{340.2}{[Cr(NH_3)_6](NO_3)_3} + 3\,HCl$$

The presence of $NaNH_2$ catalyst prevents the coproduction of $[CrCl(NH_3)_5]Cl_2$.

A hood with a good draft is needed; a one-liter Dewar flask is placed under this hood, charged with about 800 ml. of liquid NH_3, and 0.5 g. of pure Na metal and 0.2 g. of $Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$ are added. (Instead of the Dewar flask, a one-liter beaker inserted in a second, 1.5-liter beaker may also be used.) After disappearance of the blue color of the NH_3 solution, 50 g. (nearly 0.3 mole) of $CrCl_3$ is added with constant stirring (2-g. portions over a period of 1-2 hours). The brown precipitate is allowed to settle and the clear supernatant liquid is decanted or siphoned off.

The residue is transferred to a large dish and allowed to stand (with occasional stirring) until the odor of NH_3 disappears and a lustrous yellow, free-flowing powder remains. The yield of crude $[Cr(NH_3)_6]Cl_3$ is almost quantitative (about 80 g.).

The crude product is purified by dissolving rapidly in a mixture of 10 ml. of conc. HCl and 150 ml. of water at 40°C. After filtration, the solution is treated at once with 50 ml. of conc. nitric acid to precipitate pure $[Cr(NH_3)_6](NO_3)_3$. The liquid is allowed to cool to room temperature, the yellow crystalline salt is filtered on a Büchner funnel and washed with distilled water containing some HNO_3, then with alcohol, and finally with ether. The product is dried in a vacuum desiccator in the absence of light and stored in a brown bottle. Yield: 80 g. (75%).

SYNONYM:

Luteochromic chloride or nitrate.

PROPERTIES:

The chloride (as well as the nitrate) forms orange-yellow crystals, only moderately soluble in water at room temperature (the nitrate in the ratio 1:40). Solubility is still further decreased by addition of nitric acid. All $[Cr(NH_3)_6]^{3+}$ salts are sensitive to light even when dry. Decomposes slowly in solution, more rapidly on boiling, depositing chromium hydroxide. Heating with conc. HCl produces $[CrCl(NH_3)_5]Cl_2$.

REFERENCES:

I. S. M. Jörgensen. J. prakt. Chem. 30, 2 (1884).
II. A. L. Oppegard and J. C. Bailar, Jr. in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 153.

Chloropentaamminechromium (III) Chloride

$[CrCl(NH_3)_5]Cl_2$

I. BY REACTION OF LIQUID NH_3 WITH $CrCl_3$

Dry $CrCl_3$ (8 g.) is added to liquid NH_3. The reaction starts at the boiling point of the NH_3, and the $CrCl_3$ is transformed into a red

product. After evaporation of excess NH_3, the residue is triturated with 30 ml. of ice-cold water, filtered, then washed with some cold water until the filtrate is reddish. Concentrated nitric acid is added to the filtrate and $[Cr(NH_3)_6](NO_3)_3$ is obtained (see p. 1351). Yield: about 7 g.

The red residue, consisting of $[CrCl(NH_3)_5]Cl_2$, is boiled with conc. HCl, cooled, mixed with water, filtered and washed with some cold water. It is then dissolved as rapidly as possible at 50°C in 400–500 ml. of water which is acidified with a few drops of H_2SO_4. The solution is immediately filtered through a large fluted filter paper and treated with an equal volume of conc. HCl. The salt precipitates in beautiful red crystals; after one hour, these are filtered, washed with 1:1 HCl, then with alcohol, and dried in a desiccator. Yield: about 5 g.

II. FROM THE RHODOCHLORIDE BY BOILING WITH HYDROCHLORIC ACID

The procedure for the preparation of rhodochromium chloride (see p. 1359) is followed, except that after the introduction of O_2 the entire mixture is boiled for a few minutes with 2.5 times its volume of conc. HCl, whereupon the $[CrCl(NH_3)_5]Cl_2$ precipitates.

After cooling, the supernatant liquid is decanted. In 24 hours, additional purpureochromic chloride separates from the supernatant; it is, however, contaminated with NH_4Cl. The NH_4Cl is removed with dilute HCl; the residue is washed with alcohol and dried in a desiccator.

Yield: about 45 g. (from 60 g. of $K_2Cr_2O_7$).

Purification is the same as in method I (solution in water containing some H_2SO_4 and addition of HCl).

SYNONYM:

Purpureochromic chloride.

PROPERTIES:

Formula weight 243.54. Carmine-red crystals; $d_4^{15.5}$ 1.687. Solubility (16°C) 0.65 g./100 g. H_2O. In aqueous solution, even on moderate heating, adds a water molecule to give $[Cr(H_2O)(NH_3)_5]Cl_3$. Space group V_h^{15}.

REFERENCES:

I. O. T. Christensen. Z. anorg. Chem. 4, 229 (1893); H. Biltz and W. Biltz. Übungsbeispiele a. d. unorg. Exp. chemie [Exercises in Inorg. Experimental Chemistry], 3rd and 4th eds., 1920, p. 176.

II. O. T. Christensen. J. prakt. Chem. 23, 57 (1881).

Triethylenediaminechromium (III) Sulfate, Chloride and Thiocyanate

$[Cr\,en_3]_2(SO_4)_3$, $[Cr\,en_3]Cl_3 \cdot 3{,}5\,H_2O$, $[Cr\,en_3](SCN)_3 \cdot H_2O$

A) ANHYDROUS CHROMIUM (III) SULFATE

$$\underset{716.5}{Cr_2(SO_4)_3 \cdot 18\,H_2O} = \underset{392.2}{Cr_2(SO_4)_3} + 18\,H_2O$$

Heating of $Cr_2(SO_4)_3 \cdot 18\,H_2O$ for 2–3 days at 100–110°C gives a lumpy product; this is ground and dried further. Complete dehydration is indicated by the fact that the powder is no longer soluble in water.

B) ANHYDROUS ETHYLENEDIAMINE

Since anhydrous ethylenediamine attacks cork and rubber stoppers, ground glass equipment must be used. Five hundred grams of NaOH and 875 ml. of commercial ethylenediamine hydrate are heated overnight on a steam bath. Two layers form; the upper layer is decanted, treated with additional 150 g. of NaOH for several hours; the supernatant is decanted again and distilled. B.p. 116–117°C at 760 mm. Yield: almost quantitative. (Propylenediamine can be dehydrated in the same manner.)

The ethylenediamine thus obtained still contains some water. Absolutely dry ethylenediamine reacts only very slowly with the $Cr_2(SO_4)_3$.

C) TRIETHYLENEDIAMINECHROMIUM (III) SULFATE

$$\underset{392.2}{Cr_2(SO_4)_3} + 6\,\underset{360.6}{H_2N \cdot C_2H_4 \cdot NH_2} = \underset{752.8}{[Cr\,en_3]_2(SO_4)_3}$$

A 300-ml. Erlenmeyer flask, to which an air-cooled condenser is attached by a ground joint, is used to reflux 49 g. of $Cr_2(SO_4)_3$ and 50 ml. of anhydrous ethylenediamine on a steam bath. Within one hour (and often much less), the sulfate begins to lose its bright green color and its powdery nature. If this should not occur after two hours, the reaction is induced by addition of a drop of water. From this time on, the flask must be shaken to and fro, to bring unreacted $Cr_2(SO_4)_3$ into contact with the amine; the shaking is discontinued when a brown, solid mass forms; this is allowed to remain on the steam bath overnight. The solid, which is orange-yellow after cooling, is then broken up with a spatula, ground, washed with alcohol, and dried in air. Yield: 89 g. [95%, based on $Cr_2(SO_4)_3$].

D) TRIETHYLENEDIAMINECHROMIUM (III) CHLORIDE HYDRATE

$$\underset{752.8}{[Cr\ en_3]_2(SO_4)_3} + \underset{218.8}{6\,HCl} = \underset{(\cdot 3.5\,H_2O)\ 874.4}{2[Cr\ en_3]Cl_3} + 3\,H_2SO_4$$

A solution of 32 g. of $[Cr\ en_3]_2(SO_4)_3$ in dilute HCl (5 ml. of conc. HCl and 30 ml. of water) is prepared at 60–65°C and rapidly filtered through a Büchner funnel. The filtrate is stirred and cooled in ice while 27 ml. of conc. HCl is added; the chloride $[Cr\ en_3]\ Cl_3 \cdot 3.5\ H_2O$ separates at once. Filtration yields 20 g. or 60% based on the sulfate used.

This chloride is still contaminated with sulfate. It may be purified by recrystallization from water. Thus 20 g. of the crude product is dissolved in 20 ml. of water at 65°C. On cooling, 12 g. of pure chloride is obtained.

E) TRIETHYLENEDIAMINECHROMIUM (III) THIOCYANATE

$$\underset{(\cdot 3.5\,H_2O)\ 437.2}{[Cr\ en_3]Cl_3} + \underset{228.4}{3\,NH_4SCN} = \underset{(\cdot H_2O)\ 424.6}{[Cr\ en_3](SCN)_3} + 3\,NH_4Cl$$

DropBooks

A solution of 30 g. of $[Cr\ en_3]\ Cl_3 \cdot 3.5\ H_2O$ in 100 ml. of warm water is mixed, while ice-cooled and rapidly stirred, with a conc. aqueous solution of 36 g. of NH_4SCN. The sparingly soluble $[Cr\ en_3]\ (SCN)_3 \cdot H_2O$ separates at once. Filtration yields 30 g. of the crude product, or 94% based on the chloride charged.

For purification, the product is recrystallized from 100 ml. of water at 65°C, cooled, filtered, washed with alcohol and ether, and dried in air. Yield 23 g., or 77% based on the crude.

The bromide and the iodide can be obtained in exactly analogous fashion, that is, by addition of the corresponding ammonium salt.

Alternate methods: From violet chromium (III) chloride or dehydrated chrome alum, with ethylenediamine hydrate or ethylenediamine, respectively.

PROPERTIES:

The $[Cr\ en_3]^{3+}$ salts are distinctly crystalline, orange-yellow substances, which are slightly sensitive to light even when dry. Their aqueous solutions have poor stability, particularly when heated or placed in sunlight: then the initial red color is followed shortly by complete decomposition. While the sulfate is extremely soluble in water and the chloride is also very soluble, the thiocyanate, the bromide and the iodide are relatively sparingly soluble. The chloride and the thiocyanate are readily converted by

heating to the corresponding $[CrX_2\,en_2]^+$ salts (see the two preparations which follow).

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cis-Dichlorodiethylenediaminechromium (III) Chloride

$$[CrCl_2\,en_2]Cl \cdot H_2O$$

$$\underset{(\cdot 3.5\,H_2O)\ 437.2}{[Cr\,en_2]Cl_3} = \underset{(\cdot H_2O)\ 296.7}{[CrCl_2\,en_2]Cl} + H_2N \cdot C_2H_4 \cdot NH_2$$

The $[Cr\,en_2]Cl_3 \cdot 3.5\,H_2O$, which serves as the starting material, is recrystallized from a 1% aqueous NH_4Cl solution; this imparts a small NH_4Cl content to the chloride complex, and the NH_4Cl catalyzes the thermal decomposition. If the $[Cr\,en_2]Cl_3 \cdot 3.5\,H_2O$ is prepared specifically as a starting material for this reaction, the NH_4Cl may be added already during the recrystallization of the impure $[Cr\,en_2]Cl_3 \cdot 3.5\,H_2O$.

The recrystallized salt is dried and is then spread in a thin layer on a large watch glass, which is heated to 210°C. Careful control of the temperature is essential, since the rate of decomposition is too high above 215°C, while below 200°C the reaction is very slow. The evolution of ethylenediamine starts after a few minutes; the salt gradually becomes darker and after 1–2 hours turns red-violet. The course of the reaction is checked by the weight loss, which should approach the theoretical value of 30.6%.

A crude product, in satisfactory purity for many purposes, is obtained by washing with ice-cold conc. HCl. For further purification, it may be recrystallized as follows: The salt is dissolved rapidly in water at 70°C, using 4 ml. of water per gram of salt, and the filtered solution is cooled in a cooling mixture. Then 1 ml. of ice-cold conc. HCl is added for each gram of the salt, whereupon small red-violet needles separate. These are filtered and washed with alcohol and ether. Yield: 0.45 g. (60%) per gram of starting compound.

Alternate method: From $K_3[Cr(C_2O_4)_3]$ via two intermediate steps [A. Werner, Ber. dtsch. chem. Ges. 44, 3135 (1911)].

PROPERTIES:

Small red-violet needles, readily soluble in water with a violet color. The solution becomes orange after a few hours, more rapidly when warmed.

REFERENCES:

C. L. Rollinson and J. C. Bailar, Jr. in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 201; P. Pfeiffer. Ber. dtsch chem. Ges. 37, 4277 (1904); M. Linhard and M. Weigel. Z. anorg. allg. Chem. 271, 119 (1952).

trans-Dithiocyanatodi(ethylenediamine)chromium (III) Thiocyanate

$[Cr(SCN)_2\,en_2]SCN$

trans-Dichlorodi(ethylenediamine)chromium (III) Chloride

$[CrCl_2\,en_2]Cl$

a) $$\underset{(\cdot H_2O)\ 424.6}{[Cr\,en_3](SCN)_3} = \underset{348.6}{[Cr(SCN)_2\,en_2]SCN} + H_2N \cdot C_2H_4 \cdot NH_2$$

The crude $[Cr\,en_3](SCN)_3 \cdot H_2O$ used as starting material is prepared according to the directions given on p. 1355 and recrystallized from a 1% NH_4SCN solution as in the preparation of cis-$[CrCl_2\,en_2]Cl \cdot H_2O$. As in the latter case, the product is prepared by thermal decomposition, but at a temperature of 130°C (maximum 134°C). The theoretical weight loss is 16.40%. The product, which is a uniform yellow-red, is recrystallized several times from hot water, the solution concentration being such that the thiocyanate starts to crystallize slowly only after the solution is completely cold. This procedure yields 2 g. of pure $[Cr(SCN)_2\,en_2]SCN$ per 3 g. of crude; the material still contains 1-2 moles of water of hydration; this is removed in a desiccator.

b) $$\underset{346.6}{[Cr(SCN)_2\,en_2]SCN} \xrightarrow{Cl_2} \underset{278.7}{[CrCl_2\,en_2]Cl}$$

A fast stream of Cl_2 is passed through an aqueous slurry of the thiocyanate obtained in (a); good cooling is necessary. The green crystalline powder which separates from the violet solution is essentially trans-dichlorosulfate and -chloride. About 0.6 g. of this

crude dichloro salt is obtained from 2 g. of thiocyanate. A concentrated solution of the crude salt in conc. HCl is placed in an H_2SO_4 desiccator, which also contains a small dish with conc. HCl. The blue-green acid chloride $[CrCl_2\ en_2]\ Cl \cdot HCl \cdot 2\ H_2O$ (0.3 g.) separates in one day. On heating to 100°C, this is transformed into $[CrCl_2\ en_2]\ Cl$.

PROPERTIES:

Trans-$[CrCl_2en_2]Cl$ consists of green crystals. A very thin layer of a conc. aqueous solution appears green, while thicker layers have a brown-red color.

REFERENCES:

I. C. L. Rollinson and J. C. Bailar, Jr. in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 202; P. Pfeiffer, Z. anorg. Chem. 29, 113 (1902).
II. P. Pfeiffer, Ber. dtsch. chem. Ges. 37, 4282 (1904).

Dichloroaquotriamminechromium (III) Chloride

$[CrCl_2(OH_2)(NH_3)_3]Cl$

There are three position isomers: a, b, and c. The preparation starts from $(NH_3)_3CrO_4$ and hydrochloric acid.

a) One gram of $(NH_3)_3CrO_4$ (for preparation, see p. 1392) is carefully dissolved in 6 ml. of dilute HCl (the flask must be cooled with ice). It is added to the acid slowly in small portions, as soon as the vigorous reaction from the preceding portion has subsided. On addition of 10 ml. of conc. HCl and long standing in the cold, the red solution deposits red-violet snowflakelike crystals. These are recrystallized from the conc. aqueous solution by addition of conc. HCl. After washing with alcohol and ether, the crystals are dried over H_2SO_4. Yield: about 1.1 g.

b) About 2 g. of the chloride prepared in (a) is heated in HCl solution at about 60°C until the blue color of the solution is completely changed to green. By suction-filtration in a desiccator, dark green, needle-shaped crystals can be isolated from this solution; these are dried over H_2SO_4. This salt cannot be recrystallized; it is always contaminated with impurities.

c) If 8 ml. of conc. HCl is used to dissolve one gram of $(NH_3)_3CrO_4$ under the same conditions as in (a), one obtains a bright green solution, from which gray, needle-shaped crystals soon separate. These are washed with alcohol and ether and dried over H_2SO_4. Yield: about 1 g.

PROPERTIES:

Formula weight 227.50. a) Red-violet dichroic crystals, soluble in water, giving a blue color. b) Dark green, needle-shaped crystals, soluble in water, giving a green color. c) Gray, needle-shaped crystals, insoluble in cold water, soluble in warm H_2O, giving a red color.

REFERENCE:

E. H. Riesenfeld and F. Seemann. Ber. dtsch. chem. Ges. 42, 422 (1909).

Hexaureachromium (III) Chloride

$$[Cr(OCN_2H_4)_6]Cl_3 \cdot 3\,H_2O$$

$$\underset{266.5}{[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O} + \underset{360.4}{6\,OCN_2H_4} = \underset{572.8}{[Cr(OCN_2H_4)_6]Cl_3 \cdot 3\,H_2O} + 3\,H_2O$$

Green, crystalline chromium chloride hydrate $[CrCl_2(H_2O)_4]\,Cl \cdot 2\,H_2O$ and somewhat more than the stoichiometric quantity of urea are dissolved in some water and treated with a few drops of HCl. The solution is concentrated in a drying oven at 75°C (or on the steam bath) until a crystalline crust forms. The crystal slurry thus obtained is dissolved in the minimum quantity of water at 50–60°C and rapidly filtered. The salt complex separates as green needles.

PROPERTIES:

Green needles, readily soluble in water, insoluble in absolute alcohol.

REFERENCE:

E. Wilke-Dörfurt and K. Niederer, Z. anorg. allg. Chem. 184, 150 (1929).

Rhodochromium Chloride

$$[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$$

The preparation involves oxidation of an ammoniacal, NH_4Cl-containing solution of Cr (II) salt.

Sixty grams of $K_2Cr_2O_7$ powder is placed in a 2.5-liter beaker and covered with 200 ml. of conc. HCl and 75 ml. of alcohol (stirring). The resulting green solution of chromium (III) salt is reduced with zinc while still warm (but below 50°C) in the absence of air. The blue solution is poured into a mixture of 500 g. of NH_4Cl and 750 ml. of conc. ammonia, the necessary good cooling being achieved by adding pieces of ice (or by immersion in ice). After decanting from undissolved NH_4Cl, O_2 is passed through the liquid, which is shaken vigorously to achieve rapid oxidation. The liquid becomes red and rhodochloride deposits out abundantly. The salt is filtered, washed first with a mixture of 2 vol. of water and 1 vol. of conc. HCl, and then once with cold water. It is dissolved in cold water and the solution allowed to flow into a chilled mixture of 2 vol. of conc. HCl and 1 vol. of water, whereupon the rhodochloride reprecipitates almost completely. It is washes with 1:1 HCl, then with alcohol until free of acid, and dried in air in the dark. Yield: about 25 g.

PROPERTIES:

Formula weight 468.64. Pale crimson-red crystalline powder; contains 1 mole of H_2O when air-dried; this is slowly lost over conc. H_2SO_4.

REFERENCES:

S. M. Jörgensen, J. prakt. Chem. 25, 328 (1882); for composition, see K. A. Jensen, Z. anorg. allg. Chem. 232, 257 (1937), as well as W. K. Wilmarth, H. Graff and S. T. Gustin, J. Amer. Chem. Soc. 78, 2683 (1956).

Erythrochromium Chloride

$$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]Cl_5$$

Seven grams of rhodochromium chloride (preparation as above) is dissolved in 50 ml. of 2 N ammonia. This blue solution becomes pure crimson red in about 15 minutes; it is then cooled in ice and treated with 100 ml. of ice-cold, conc. HCl. The erythrochloride which precipitates is filtered, washed with some dilute HCl, then with alcohol and ether, and dried over H_2SO_4. Yield: 95%.

PROPERTIES:

Light-sensitive, crimson-red crystalline powder; more readily soluble in water than the rhodochloride.

REFERENCES:

K. A. Jensen. Z. anorg. allg. Chem. 232, 264 (1937). W. K. Wilmarth, H. Graff and S. T. Gustin. J. Amer. Chem. Soc. 78, 2683 (1956).

Tris(2,2'-dipyridyl)chromium (II) Perchlorate

$$[Cr(dipy)_3](ClO_4)_2$$

$$\underset{52}{Cr} + 2\,HCl = \underset{(\cdot aq.)}{CrCl_2} + H_2$$

$$\underset{(\cdot aq.)}{CrCl_2} + 3\ \underset{468}{dipy} = \underset{(\cdot aq.)}{[Cr(dipy)_3]Cl_2}$$

$$\underset{(\cdot aq.)}{[Cr(dipy)_3]Cl_2} + 2\,NaClO_4 = \underset{719}{[Cr(dipy)_3](ClO_4)_2} + 2\,NaCl$$

All operations are carried out under pure N_2 and with deaerated liquids.

A solution of 0.26 g. of electrolytic Cr (preparation on p. 1335) in 2.5 ml. of 1 : 1 HCl is prepared. After the H_2 evolution ceases, the solution is diluted with 20 ml. of water, and 2.35 g. of 2,2'-dipyridyl, dissolved in some methanol, is added. The solution, now a deep wine-red, is filtered through a fine fritted-glass filter. The filtrate is treated with a solution of 1 g. of $NaClO_4$ and 0.5 ml. of 70% $HClO_4$ in 50 ml. of water. A slurry of black-violet crystals is formed at once. This is filtered on fine fritted glass, washed with water, alcohol and ether, and dried in vacuum over P_2O_5. Yield: 3 g. (83% of theory).

PREPARATION OF 2,2'-DIPYRIDYL

a) From $FeCl_3$ and pyridine in an autoclave [F. Hein and H. Schwedler, Ber. dtsch. chem. Ges. 68, 681 (1935)]; *b*) refluxing of Raney nickel and pyridine [G. M. Badger and W. H. F. Sasse, J. Chem. Soc. (London) 1956, 616].

The corresponding complexes with 1,10-phenanthroline $[Cr\ phen_3]_n\ X_n$ (where X = I or ClO_4 and n = 1, 2, 3) can be prepared in a similar manner [S. Herzog, Chem. Techn. 8, 544 (1956)].

PROPERTIES:

Small black crystals; completely stable in air when dry, but oxdidized when damp (acquires a yellow color). Sparingly soluble in water or methanol, giving an intense wine-red color.

insoluble in ether and benzene. In weak perchloric acid solution oxidized by air, forming yellow *tris*(2,2′-dipyridyl)chromium (III) perchlorate, which can be crystallized by concentrating the solution in the cold over H_2SO_4.

REFERENCES:

S. Herzog. Thesis, Univ. of Jena, 1952; F. Hein and S. Herzog. Z. anorg. allg. Chem. 267, 337 (1952); G. A. Barbieri and A. Teitamanzi. Atti R. Accad. Lincei (Rome), Rend. [6] 15, 877 (1932).

Tris(2,2'-dipyridyl)chromium (I) Perchlorate

$[Cr(dipy)_3]ClO_4$

$$\underset{2\cdot710}{2\,[Cr(dipy)_3](ClO_4)_2} + Mg = \underset{2\cdot610}{2\,[Cr(dipy)_3]ClO_4} + Mg(ClO_4)_2$$

All operations are carried out under pure N_2 and with air-free liquids.

Tris(2,2′-dipyridyl)chromium (II) perchlorate (1.0 g.; preparation as above) is covered with 250 ml. water, giving an opaque wine-red solution. This is treated with 60 mg. of Mg powder (about 3 times the stoichiometric quantity) and machine-shaken in a well-closed container. The solution becomes colorless after a maximum of 3 hours, and a fine, indigo-colored powder separates out. The powder, because of its fine particle size, imparts an apparent black-violet color to the solution on superficial examination. Now 3 g. of NH_4ClO_4 is added and the mixture is shaken for an additional hour to dissolve the remaining Mg. After standing overnight, the dark-blue product is filtered through a fine fritted-glass filter, washed three times with 5-ml. portions of water, and dried in vacuum over P_2O_5. After a few hours, the preparation is dust-dry. Yield: about 0.65 g. (about 80% of theory).

PROPERTIES:

Indigo-blue powder; soluble in methanol, ethanol, acetone and pyridine, giving a deep, inky blue color; insoluble in water, benzene and ether. The solution is oxidized almost instantly in air, becoming lighter in color. The dry product reacts spontaneously with atmospheric O_2 with considerable evolution of heat and loss of the 2,2′-dipyridyl.

REFERENCES:

S. Herzog. Thesis, Univ. of Jena, 1952. F. Hein and S. Herzog. Z. anorg. allg. Chem. 267, 337 (1952).

Tris(2,2'-dipyridyl)chromium (0)

$[Cr(dipy)_3]$

$$\underset{(\cdot 2\,H_2O)\ 376.2}{Cr_2(CH_3COO)_4} + \underset{468.6}{3\ dipy} = \underset{520.6}{[Cr(dipy)_3]} + Cr(III)\ \text{and}\ Cr(II)\ \text{complexes.}$$

Two grams of chromium (II) acetate hydrate is mixed (in the absence of air) with 2.49 g. of 2,2'-dipyridyl (equivalent to 1.5 moles of dipyridyl per g.-atom of Cr). Now, 40 ml. of deaerated water is added and the resulting suspension is machine-shaken for three hours. The black precipitate is filtered off from the deep-red mother liquor (through a very fine fritted-glass filter), washed with water and alcohol, and dried over air-free P_2O_5. Yield: about 1 g.

Alternate methods: Reduction of *tris*(2,2'-dipyridyl)chromium (II) salt in tetrahydrofuran with sodium.

PROPERTIES:

Small black crystals; soluble in benzene, tetrahydrofuran, pyridine or dimethylformamide with a red color. Ignites in air with oxidation to Cr_2O_3.

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REFERENCE:

S. Herzog, K. Chr. Renner and W. Schön. Z. Naturforsch. 12b, 609 (1957).

Hexaphenylisonitrilochromium (0)

$[Cr(C_6H_5NC)_6]$

$$\underset{1128.7}{3\,Cr_2(CH_3COO)_4 \cdot 2\,H_2O} + C_6H_5NC\ (\text{excess}) \rightarrow$$

$$\underset{1241.4}{2\,[Cr(C_6H_5NC)_6]} + 4\,Cr(III)\ \text{complex}$$

The reaction is carried out under N_2; a large excess of phenyl isonitrile is desirable. Six grams of chromium (II) acetate $Cr_2(CH_3COO)_4 \cdot 2\,H_2O$ is suspended in 40 ml. of methanol, and a solution of 20 g. of isonitrile in 10 ml. of methanol is added. After about one hour, well-formed garnet-red crystals separate from the deep black-red solution. The precipitate is filtered, washed with some methanol, and dried.

The yield is 5-6 g., which is almost quantitative, based on the disproportionation shown above.

PROPERTIES:

Garnet-red crystals with metallic, yellowish-green reflectance, stable in air, diamagnetic. M.p. 178.5°C (undergoes deformation at 151°C). Soluble in chloroform and benzene in the cold, readily soluble in the hot solvents. Can be recrystallized by reprecipitation with alcohol from a chloroform solution. Can be obtained from methylene chloride; in this case, large crystals, similar in appearance to pyrites, are obtained.

REFERENCE:

L. Malatesta, A. Sacco and S. Ghielmi. Gazz. Chim. Ital. 82, 516 (1952).

If a Cr (II) halide is used instead of the Cr (II) acetate, the reaction is completely different: a crystalline precipitate of $[Cr(RNC)_4Cl_2]$ (orange-red) or $[Cr(RNC)_4Br_2]$ (olive brown), depending on the starting halide used, forms instantly. These compounds show a paramagnetism of 2.84 Bohr magnetons, corresponding to Cr^{2+}. They are again completely stable in air and can even be heated in water without decomposition; insoluble in ether, alcohol, benzene and carbon tetrachloride, but soluble in chloroform and methylene dichloride.

REFERENCE:

F. Hein and W. Kleinwächter. Private communication, unpublished.

Chromium Orthophosphate

$CrPO_4$

$$\underset{400.0}{4\,CrO_3} + \underset{392.0}{4\,H_3PO_4} + \underset{150.2}{3\,N_2H_4\cdot H_2O} = \underset{588.0}{4\,CrPO_4} + \underset{270.2}{15\,H_2O} + \underset{67.2\,l.}{3\,N_2}$$

A mixture of 11.6 g. of 85% H_3PO_4 (d 1.69), 12.5 g. of CrO_3 (125% of the stoichiometric quantity) and 200 ml. of H_2O is prepared, and 5.4 g. of 80% hydrazine hydrate (115% of the stoichiometric amount) in 100 ml. of H_2O is added in drops and with stirring. After stirring for 15 minutes at 50°C, the precipitate is washed, suction-dried, and then dried for 2 hours at 100°C. Yield: 19 g. of amorphous

3.5-hydrate. Heating for 2 hours in vacuum at 800°C yields 13 g. of $CrPO_4$, which gives a crystalline x-ray diffraction pattern.

PROPERTIES:

Hydrate: Turquoise green powder. d 2.15. Following the above directions gives a particle size of 0.1 μ, while a tenfold dilution of the reactants gives 1-μ particles.

Anhydrous: Gray-brown; insoluble in H_2O and CH_3COOH. d 3.05.

REFERENCES:

F. Wagenknecht. German Patents 1,046,597 (1957) and 1,056,104 (1957).

Chromium (II) Sulfate

$CrSO_4 \cdot 5\,H_2O$

$$\underset{52.0}{Cr} + \underset{98.1}{H_2SO_4} + \underset{90.1}{5\,H_2O} = \underset{236.2}{CrSO_4 \cdot 5\,H_2O} + \underset{2.0}{H_2}$$

Twenty grams of coarse, very pure electrolytic chromium (>99.99% Cr) is placed in 150 ml. of H_2O, and 46 g. of conc. H_2SO_4 is then added with agitation. The Cr is completely dissolved and massive crystals of $CrSO_4 \cdot 5\,H_2O$ precipitated from the deep blue, highly supersaturated solution. Concentration of the liquid in vacuum gives an almost theoretical yield of the product. The salt is filtered, washed with some ice-cold water, and dried in vacuum or in a stream of N_2; any water present can be removed by thorough washing with acetone.

PROPERTIES:

Blue, massive crystals. Completely stable in air when dry. Solutions are instantly oxidized on contact with atmospheric O_2. Solubility (0°C): 21 g./100 g. H_2O. Isotypic with $CuSO_4 \cdot 5\,H_2O$.

REFERENCE:

H. Lux and G. Illmann. Chem. Ber. 91, 2143 (1958).

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Chromium (II) Salt Solutions

I. PREPARATION BY ELECTROLYTIC REDUCTION

$$\underset{294.2}{K_2Cr_2O_7} + 3\,SO_2 + \underset{98.1}{H_2SO_4} \rightarrow K_2SO_4 + \underset{392.2}{Cr_2(SO_4)_3}\ (\text{aq})$$

$$\underset{392.2}{Cr_2(SO_4)_3}\ (\text{aq}) + 2\ e \rightarrow 2\,\underset{296.1}{CrSO_4}\ (\text{aq}) + SO_4^{--}$$

The electrolysis apparatus (see Fig. 318) comprises a 1.5-liter jar p and a cylindrical porous clay cell q of about 500-ml. capacity (height 17 cm., diameter 6.5 cm.); the cell is closed off with a rubber stopper which carries a glass stirrer u with a mercury seal, a sampling tube s, a gas outlet tube t, and a lead cathode v having 230 $cm.^2$ of surface. The cell is surrounded by the Pb anode w.

The Pb cathode should be prepared according to directions given by Tafel (see the references below). It is suspended in 20% sulfuric acid and surrounded coaxially by a second cylindrical Pb electrode. The current (0.13 amp./$in.^2$) is turned on, and the working electrode is operated first as an anode, then as a cathode (5 min.), and finally again as an anode (15 min.). After this, it is brown. It is washed with boiling water and dried.

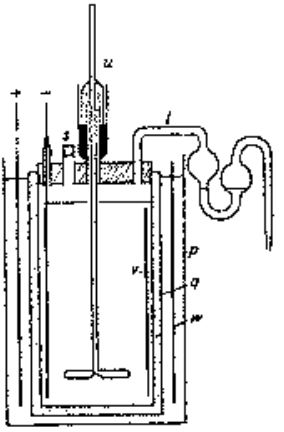

Fig. 318. Preparation of chromium (II) sulfate by electrolytic reduction. p jar; q porous clay cell; s sampling tube; t gas outlet tube; u stirrer with Hg seal; v lead cathode; w lead anode.

The chromium (III) sulfate solution required for the electrolytic reduction is prepared as follows: SO_2 is bubbled through a solution of 80 g. of $K_2Cr_2O_7$, 30 g. of conc. H_2SO_4 and 450 g. of water until reduction is complete. Good cooling is necessary to prevent the transformation of violet to green chromium (III) sulfate [the latter is not as readily reduced to chromium (II) sulfate]. The excess SO_2 is driven off with a fast stream of air. The last traces of SO_2 must be removed by brief boiling. The solution, whose volume is now about 50 ml., is transferred to the clay cell. The anodic electrolyte is 2 N H_2SO_4. Electrolysis proceeds at a current density of 0.13 amp./$in.^2$, that is, at a current of 4.6 amp. The reduction takes 12 hours, but up to 24 hours may be required if a great deal of green chromium (III) sulfate is present. The course of the reduction can be followed by

removing samples and titrating with excess 0.1 N $KMnO_4$, adding KI, and back-titrating with 0.1 N $Na_2S_2O_3$.

II. PREPARATION BY REDUCTION WITH ZINC

It is best to use a zinc reductor. This consists of a vertical glass tube, 45 cm. long and 2 cm. I.D., with a glass stopcock at the lower end. It is two-thirds filled with zinc granules. Before use the contents of the column are amalgamated for 10 minutes with a 0.1 M $HgCl_2$ solution in 1 M HCl, then washed with a large quantity of water and finally with some 1 N H_2SO_4; during this operation the liquid level should always be above the zinc. The reduction proper is carried out by adding a solution of 90 g. of green chromium (III) chloride hydrate in 120 ml. of water and 30 ml. of 2 N H_2SO_4 to the reductor tube; the rate of discharge from the reductor is so adjusted that only a pure, light blue chromium (II) salt solution drops into the directly attached storage or reaction vessel.

This solution obviously contains zinc salts. Solutions completely free of foreign salts are obtained either by dissolving chromium (III) acetate or, better, by dissolving electrolytic chromium in dilute HCl, as described, for example, in the procedure for *tris*(2,2′-dipyridyl)chromium (II) perchlorate.

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APPLICATIONS

Useful for removing O_2 from gases, for reductometric titration, and as a reductant in organic chemistry.

PROPERTIES:

Blue solution, very sensitive to air; storage stability is highly dependent on the purity of the starting materials.

REFERENCES:

I. Ch. W. Hofmann. Thesis, Univ. of Bern, 1947; R. Flatt and F. Sommer. Helv. Chim. Acta 25, 684 (1942); A. Asmanow. Z. anorg. allg. Chem. 160, 210 (1927); W. Traube and A. Goodson. Ber. dtsch. chem. Ges. 49, 1679 (1916); J. Tafel. Z. phys. Chem. 34, 187 (1900).

II. E. Zintl and G. Rienäcker. Z. anorg. allg. Chem. 161, 378 (1927); M. R. Hatfield in: L. F. Audrieth, Inorg. Syntheses, Vol III, New York-Toronto-London, 1950, p. 149.

Chromium (II) Acetate

$Cr_2(CH_3COO)_4 \cdot 2\,H_2O$

I.

$$\underset{(\cdot 6\,H_2O)\ 266.5}{CrCl_3} + {}^1/_2\,Zn = \underset{(\cdot aq)}{CrCl_2} + {}^1/_2\,ZnCl_2\ \ 32.7$$

$$\underset{(\cdot aq)}{CrCl_2} + 2\,\underset{(\cdot 3\,H_2O)\ 272.2}{Na(CH_3COO)} = {}^1/_2\,\underset{(\cdot 2\,H_2O)\ 188.1}{Cr_2(CH_3COO)_4} + 2\,NaCl$$

Pure chromium (II) acetate may be prepared only if oxygen is completely excluded. This condition is approached in the apparatus of Fig. 319.

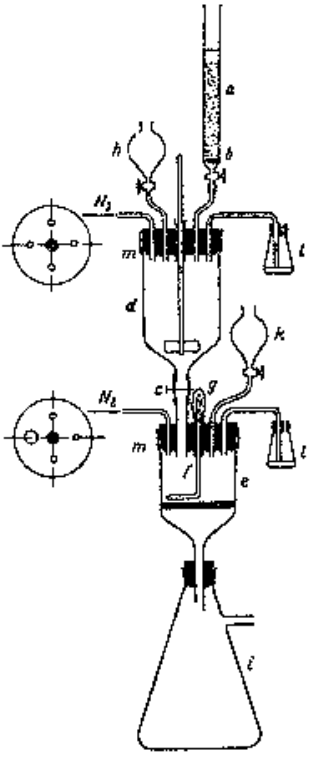

Fig. 319. Preparation of chromium (II) acetate. *a* zinc reductor; *b* glass wool plug; *c* pinchcock or glass stopcock with 10-mm. bore; *d* reaction vessel; *e* fritted-glass funnel; *f* glass stirrer; *g* rubber cap to seal stirrer against outside air; *h* dropping funnel; *i* suction flask; *k* dropping funnel for washing liquids; *l* bubble trap for outgoing inert gas; *m* rubber sleeve for sealing large stopper.

The chromium (II) salt solution is obtained in a Zn reductor (see previous preparation). This consists of a glass tube *a* (45 cm. long and 2 cm. I.D.) in which a glass wool plug is inserted at *b*. The Zn granules filling the tube are amalgamated before use

(10 minutes with a 0.1 M $HgCl_2$ solution in 1 M HCl), then washed with large quantities of water and finally with some 1 N H_2SO_4; during this procedure the liquid level should always be above the zinc. A pinchcock or a glass stopcock with a 10-mm. bore is located at *c*. Reaction vessel *d* is attached with a rubber tube to the moderately coarse fritted-glass funnel *e* (diameter about 10 cm.). Glass stirrer *f* should provide thorough stirring of the precipitate during the washing and drying steps; it is held in place and turned by means of the rubber cap *g* which serves as a seal. Nitrogen or carbon dioxide (O_2-free) is passed through the reaction vessel during the precipitation, and over the precipitate during the filtration. The gage pressure in the apparatus (governed by the liquid height in the trap *l*) should be as small as possible.

A solution of 90 g. of green chromium (III) chloride hydrate in 120 ml. of water and 30 ml. of 2 N H_2SO_4 is poured into the reductor tube and its outflow rate so adjusted that only a pure light blue chromium (II) salt solution drops into the reaction vessel *d*. A filtered solution of 252 g. of Na acetate in 325 ml. of water is charged beforehand into the reaction vessel (via *h*). During the precipitation the vessel contents are stirred briefly by hand, using the stirrer provided.

After completion of the precipitation, N_2 or CO_2 is admitted into filter *e* and stopcock *c* is opened. In this operation the filtering flask *i* can be carefully put under a slight vacuum, provided a sufficient flow of N_2 (or CO_2) is maintained and the chromium (II) acetate is always surrounded only by the protective gas. The precipitate is washed on the filter with air-free distilled water, then several times with alcohol, and finally with peroxide-free ether, after which N_2 or CO_2 (H_2O-free) is passed through for 24 hours. The chromium (II) acetate must be completely dry before it can be exposed to air, since it oxidizes at an appreciably faster rate when moist. Yield: 55 g.

The preparation can also be carried out with smaller quantities, e.g., one third of those given above. In this case, the dimensions are reduced to 7 cm. I.D. for the precipitating vessel *d* and the funnel *e*. The reductor need be only 35 cm. high (filled to 25 cm.). The drawing of Fig. 318 is based on dimensions appropriate to this case.

II. $$\underset{52.0}{Cr} + 2\,HCl \rightarrow CrCl_2 \cdot aq.$$

$$CrCl_2 \cdot aq. + 2\,CH_3COONa \rightarrow \underset{(\cdot 2\,H_2O)\ 188.1}{{}^1/_2\,Cr_2(CH_3COO)_4} + 2\,NaCl$$

Two grams of electrolytic chromium is covered with a mixture of 6.2 ml. of conc. HCl and an equal volume of water (air should be

excluded). After the start of the H_2 evolution, about 10 additional ml. of water is added and the vessel is heated on a steam bath. When the evolution of H_2 ceases, the sky-blue solution of chromium (II) chloride is slowly filtered through a fine fritted-glass funnel into a solution of 28 g. of sodium acetate in 40 ml. of deaerated water. The solution immediately turns red, and after a few seconds small glittering red crystals begin to precipitate. After overnight standing, these are filtered through fine fritted glass, washed five times with 10-ml. portions of water, dried with air-free $CaCl_2$, and stored under N_2. Yield: about 6 g.

Other means of obtaining chromium (II) salt solutions may be used instead of direct solution of the chromium used, provided the product solutions contain no foreign substances which would affect the precipitation of the acetate.

PROPERTIES:

Dark-red crystals, slightly soluble in water and alcohol. Insoluble in ether. When dry, stable in air for a few hours; stable indefinitely under N_2. Drying over P_2O_5 at 100°C results in loss of the complexed water, change of color to brown, and increased sensitivity to air.

REFERENCES:

S. Vanino, Handb. d. präp. Chemie [Handbook of Preparative Chemistry], Inorg. Section, Stuttgart, 1925, p. 710; E. Zintl and G. Rienäcker, Z. anorg. allg. Chem. 161, 378 (1927); M. R. Hatfield in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 149; K. H. Zapp, Unpublished, Freiburg i. Br.; S. Herzog, Unpublished, Jena; M. Kranz and A. Witkowska, Przemysl Chem. 37, 470 (1958); Inorg. Syntheses, Vol. VI, 1960, p. 144.

Chromium (II) Oxalate

$$CrC_2O_4 \cdot 2\,H_2O$$

$$\underset{238.2}{CrSO_4 \cdot 5\,H_2O} + \underset{134.0}{Na_2C_2O_4} = \underset{176.1}{CrC_2O_4 \cdot 2\,H_2O} + \underset{142.1}{Na_2SO_4} + \underset{54.0}{3\,H_2O}$$

A dry mixture of 14 g. of $CrSO_4 \cdot 5\,H_2O$, 8 g. of $Na_2C_2O_4$, and 0.25 g. of $H_2C_2O_4 \cdot 2\,H_2O$ is covered with about 150 ml. of O_2-free H_2O under a protective blanket of N_2. This mixture is shaken vigorously. After some time, $CrC_2O_4 \cdot 2\,H_2O$ separates as a fine, crystalline, green precipitate. It is filtered, washed with cold H_2O,

and dried over $CaCl_2$, giving a yellowish-green powder. The yield is 80–85%.

Alternate method: Reaction of solid $Na_2C_2O_4$ with concentrated solutions of chromium (II) salt obtained electrolytically (method of Walz).

REFERENCES:

H. Lux and G. Illmann. Chem. Ber. 91, 2143 (1958); H. Walz. M.S. thesis, Univ. of Freiburg i. Br., 1958.

Hexaaquochromium (III) Acetate

$[Cr(OH_2)_6](CH_3COO)_3$

$$\underset{157.1}{Cr(OH)_3 \cdot 3\,H_2O} + 3\,\underset{180.2}{CH_3COOH} = \underset{337.2}{[Cr(H_2O)_6](CH_3COO)_3}$$

I. Excess glacial acetic acid is added to the light blue-green A-chromium (III) hydroxide (for preparation see p. 1345). The reaction proceeds with appreciable evolution of heat. The crystals (which precipitate after a few hours) are separated from the mother liquor, washed thoroughly with acetone and ether, and dried over H_2SO_4.

II. *Alternate method:* From chrome alum via the readily obtained dihydroxotetraaquochromium (III) sulfate.

PROPERTIES:

Needle-shaped blue-violet crystals, readily soluble in water; solvolyzed by alcohol.

REFERENCES:

I. A. Hantzsch and E. Torke. Z. anorg. allg. Chem. 209, 78 (1932).
II. A. Werner. Ber. dtsch. chem. Ges. 41, 3452 (1908).

Dihydroxohexaacetatotrichromium (III) Acetate and Chloride

$[Cr_3(OH)_2(CH_3COO)_6](CH_3COO) \cdot n\,H_2O$, $[Cr_3(OH)_2(CH_3COO)_6]Cl \cdot 8\,H_2O$

Prepared from CrO_3, glacial acetic acid and alcohol.

a) A two-liter round-bottom flask fitted with a reflux condenser is used. It is charged with 200 g. of CrO_3 (sulfuric acid-free),

which is then covered with 400 ml. of commercial glacial acetic acid. The reaction is induced by careful heating on a water bath which is held below the boil. Since pure CrO_3 does not react with very pure glacial acetic acid even at the boil, the reaction may be started by addition of some alcohol. If the reaction becomes too vigorous, the flask is cooled. When the evolution of CO_2 begins to subside, the flask contents are refluxed for about 2 hours on a rapidly boiling water (or steam) bath. The thick, brown contents of the flask, which consist of hexaacetatotrichromium chromates, are allowed to cool somewhat. To complete the reduction of any chromic acid still present, first 50% alcohol and then 96% alcohol (about 100 ml. of alcohol in all) is added in small portions through the condenser. The flask is now heated for one hour on a steam bath, and the green liquid is then concentrated on a water bath. The green diacetate powder has the formula

$$[Cr_3OH(H_2O)(CH_3COO)_6](CH_3COO)_2 \cdot H_2O.$$

The monoacetate hexahydrate is obtained by dissolving the powder in some water and allowing evaporation to take place over H_2SO_4. The monoacetate tetrahydrate crystallizes in long prisms when an aqueous solution of the diacetate is treated with acetone.

PROPERTIES:

Formula weight 675.41 (4 H_2O), 711.45 (6 H_2O). Green, water-soluble crystals.

b) Evaporation of a solution of the diacetate in dilute HCl over H_2SO_4 yields $[Cr_3(OH)_2(CH_3COO)_6]Cl \cdot 8\ H_2O$.

PROPERTIES:

Formula weight 723.90. Dark green prisms, may be recrystallized from water.

REFERENCES:

R. F. Weinland and E. Büttner. Z. anorg. allg. Chem. 75, 329, Anm. 1 (1912); R. Weinland and P. Dinkelacker. Ber. dtsch. chem. Ges. 42, 3010, 3012 (1909).

Potassium Trioxalatochromate (III)

$$K_3[Cr(C_2O_4)_3] \cdot 3\ H_2O$$

Prepared by treatment of oxalic acid and potassium oxalate with $K_2Cr_2O_7$.

A concentrated aqueous solution containing 12 g. $K_2Cr_2O_7$ is added dropwise with stirring to a solution containing 27 g. of oxalic acid dihydrate and 12 g. of neutral potassium oxalate monohydrate. The mixture is then evaporated to a small volume and slowly cooled to bring about crystallization.

SYNONYM:

Potassium chromium oxalate.

PROPERTIES:

Formula weight 485.4. Black-green, monoclinic scales with transparent blue edges. Readily soluble in water.

REFERENCE:

H. Hecht. Präparative anorg. Chemie [Preparative Inorganic Chemistry], Berlin-Göttingen-Heidelberg, 1951, p. 158.

Potassium Hexacyanochromate (III)

$$K_3[Cr(CN)_6]$$

$$Cr(CH_3COO)_3 + 6\,KCN \rightarrow K_3[Cr(CN)_6] + 3\,CH_3COOK$$

DropBooks

Seventeen grams of CrO_3 or 25 g. of $K_2Cr_2O_7$ is treated with 70 ml. of HCl (45 ml. of conc. HCl + 25 ml. of water) and reduced while hot by addition of a total of 25 ml. of ethanol in small portions. A very slight excess of ammonia is added to the boiling solution. The precipitate of $Cr(OH)_3$ is filtered hot through a fluted filter paper, washed several times with hot water, and finally dissolved in some dilute acetic acid. This solution is evaporated almost to dryness in order to remove the excess acetic acid. The residue is taken up in 150 ml. of water, filtered, and poured into a boiling solution of 100 g. of KCN in 200 ml. of water (use a hood!). The very dark-red solution thus formed is evaporated on a steam bath. A brownish-black solid usually separates; this is removed by filtration. On further concentration, bright-yellow crystals deposit on the walls. The mother liquor also yields additional fractions. The product is recrystallized two or three times from water and dried over H_2SO_4. The yield is 38 g. (70%).

PROPERTIES:

Formula weight 325.41. d 1.71. Bright yellow, monoclinic crystals, isomorphous with $K_3[Fe(CN)_6]$; decomposes above 150°C. Solubility at 20°C: 30.96 g./100 g. water; insoluble in alcohol and

Aqueous solutions tend to decompose, especially in light or on heating, separating $Cr(OH)_3$.

REFERENCES:

F. V. D. Cruser and E. H. Miller. J. Amer. Chem. Soc. 28, 1133 (1906); O. T. Christensen. J. prakt. Chem. [2] 31, 163 (1885); see also J. H. Bigelow in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 203.

Potassium Hexathiocyanatochromate (III)

$$K_3[Cr(SCN)_6] \cdot 4\,H_2O$$

$$\underset{\cdot 12\,H_2O}{KCr(SO_4)_2} + 6\,KSCN = \underset{\cdot 4\,H_2O}{K_3[Cr(SCN)_6]} + 2\,K_2SO_4$$

499.4 583.0 589.8

A moderately concentrated aqueous solution of 6 parts of KSCN and 5 parts of chrome alum is heated for 2 hours on a steam bath, and is then concentrated in a dish until the cooled residual liquid solidifies to a mass of red crystals. This solid is extracted with absolute alcohol, in which the $K_3[Cr(SCN)_6]$ dissolves very readily while K_2SO_4 remains as a residue. After evaporation of the filtered alcohol extract, the salt is recrystallized once more from alcohol.

The analogous ammonium salt $(NH_4)_3[Cr(SCN)_6] \cdot 4\,H_2O$ is obtained in the same manner, except that reaction in the solution of NH_4SCN and chromium ammonium alum takes place only after a brief period of boiling.

SYNONYM:

Potassium chromium thiocyanate.

PROPERTIES:

Lustrous crystals; dark red-violet in reflected light and garnet red in transmitted light. The salt remains unchanged in air or over H_2SO_4; it loses its water of crystallization only when heated to 110°C. One part dissolves in 0.72 parts of water and in 0.94 parts of alcohol; d^{16} 1.711.

REFERENCE:

J. Roesler. Liebigs Ann. 141, 185 (1867).

Trilithium Hexaphenylchromate (III)

$$Li_3Cr(C_6H_5)_6 \cdot 2.5(C_2H_5)_2O$$

$$\underset{158.4}{CrCl_3} + 6\,\underset{504.2}{Li(C_6H_5)} \xrightarrow{\text{ether}} \underset{720.5}{Li_3Cr(C_6H_5)_6 \cdot 2.5\,(C_2H_5)_2O} + 3\,\underset{127.3}{LiCl}$$

All operations are conducted in the absence of air and moisture, using high-purity N_2 as a protective gas.

a) The required solution of phenyllithium is prepared in a 500-ml. three-neck flask fitted with a reflux condenser and Hg seal, a high-speed Hg-sealed mechanical stirrer, a gas inlet tube, and a dropping funnel. The procedure is as follows: Clean, finely cut lithium (6 g.) is covered with 100 ml. of ether that has been freshly distilled over benzophenonesodium (referred to hereafter as ketyl ether). With the stirrer operating at high speed, 64 g. of freshly distilled bromobenzene, dissolved in 200 ml. of ketyl ether, is added dropwise at a rate sufficiently fast to keep the reaction solution boiling vigorously. After all the bromobenzene has been added, the solution is refluxed for one hour. After cooling, it is filtered through fine fritted glass. The clear solution thus obtained has a phenyllithium concentration of about 10%.

b) The preparation of the lithium chromium phenyl complex employs the same apparatus as described in (a). However, the dropping funnel is replaced by a tap-injection bulb containing 10 g. of anhydrous, very finely powdered chromium (III) chloride. With vigorous, high-speed stirring of the lithium phenyl solution in the flask, the chromium chloride is slowly introduced by tapping the bulb. The course of the reaction is monitored by observing the decrease in the number of black particles of chromium chloride. After 10-12 hours, the reaction is discontinued without waiting for complete conversion of the solid chromium chloride. The nascent yellow precipitate is filtered through fine fritted glass. By cooling the black-brown filtrate to −10°C, a portion of the complex is obtained in beautiful crystals. The reaction residue is rinsed back into the three-neck flask with 200 ml. of ketyl ether and again collected on the fritted glass.

The reaction flask is now replaced with a reflux condenser which is attached to the N_2-generating apparatus (to equalize the pressure). The receiver flask is heated and the ether is distilled through the fritted glass plate and onto the residue; by cooling the receiver flask, the ether is suction-drawn through the residue back into the flask. This operation is repeated until the residue is colorless. On cooling, most of the complex compound crystallizes in the receiver. The crystal slurry thus obtained is recrystallized from a large quantity of ketyl ether; or it is extracted

DropBooks

with fresh ketyl ether as described above. The mother liquor must be yellow-brown and free of halogens. Yield: about 15 g.

PROPERTIES:

Yellow-orange crystals; soluble in ether, benzene and tetrahydrofuran; sensitive to air and moisture; completely hydrolyzed by water or alcohol.

REFERENCE:

F. Hein and R. Weiss. Z. anorg. allg. Chem. 295, 145 (1958).

Ammonium Tetrathiocyanatodiamminechromate (III)

$$NH_4[Cr(SCN)_4(NH_3)_2] \cdot H_2O$$

Prepared by fusion of NH_4SCN with $(NH_4)_2Cr_2O_7$ and extraction with water.

An enamel cooking pot of at least 4-liter capacity is charged with 800 g. (10.5 moles) of NH_4SCN and carefully heated; several small flames are used to provide as uniform heating as possible. The mass is stirred with a glass test tube which contains a thermometer; the heating is continued until the solid is partly melted and the temperature is 145–150°C. Now, an intimate mixture of 170 g. (0.675 mole) of finely powdered $(NH_4)_2Cr_2O_7$ and 200 g. (2.6 moles) of NH_4SCN is added in portions of 10–12 g. with continuous stirring. A fairly vigorous reaction begins after 10 such portions have been added; NH_3 is evolved and the temperature rises to 160°C. The flames are now extinguished and the rest of the mixture is added to the melt in such a way as to maintain the temperature at 160°C.

Stirring is continued as the melt cools; the solid product which deposits on the walls of the vessel is scraped away, ground to a fine powder while still warm, and stirred in a large beaker with 750 ml. of ice water. After 15 minutes, the insoluble residue is freed of mother liquor as completely as possible (suction-filtration, no washing). It is then stirred into 2.5 liters of water, preheated to 65°C. The temperature is rapidly restored to 60°C and the solution is filtered all at once through a funnel heated with hot water (heating above 65° causes rapid decomposition, with production of a blue color and generation of HCN).

The hot filtrate is placed overnight in an ice chest, and the separated crystals are then filtered with suction. The mother liquor is used for another extraction of the residue at 60°C, thus affording an additional quantity of crystalline Reinecke salt.

Finally, 12–13 additional grams of product may be obtained by concentrating the mother liquor to 250–300 ml. under reduced pressure at 40–50°C.

The total yield of air-dry Reinecke salt amounts to 250–275 g. (52–57% of theory).

The insoluble residue from the second extraction (about 130–135 g.) is composed predominantly of Morland salt, i.e., guanidium tetrathiocyanatodiamminechromate (III).

USES:

Used for the isolation of amines, amino acids, complex cations and organometallic bases; it forms sparingly soluble salts with all of the above; these salts usually crystallize well. Also used as reagent in quantitative determination of Cu and Hg (procedure of C. Mahr) and of quaternary onium cations (procedure of F. Hein).

SYNONYM:

Reinecke salt.

PROPERTIES:

Formula weight 354.45. Ruby-red, lustrous, light-sensitive leaflets, which lose their water of crystallization on drying at 100°C and form scarlet cubes and rhombododecahedra. Both forms are readily soluble in cold water, alcohol, acetone and moist ethyl acetate, insoluble in benzene. Decomposed by boiling water.

DropBooks

REFERENCES:

H. D. Dakin. Org. Syntheses 15, 74 (1935); Coll. Vol. II, 555 (1943).

Tetrathiocyanatodiamminechromic (III) Acid

$$H[Cr(SCN)_4(NH_3)_2]$$

$$\underset{(\cdot H_2O)\ 354.5}{NH_4[Cr(SCN)_4(NH_3)_2]} + \underset{36.5}{HCl} = \underset{(\cdot 2H_2O)\ 355.4}{H[Cr(SCN)_4(NH_3)_2]} + NH_4Cl$$

A concentrated aqueous solution of $NH_4[Cr(SCN)_4(NH_3)_2] \cdot H_2O$ (see preceding preparation) is treated with a small excess of hydrochloric acid, then extracted thoroughly with ether. The free acid is absorbed in the ether with an intense dark red color; addition of NaCl makes the extraction almost quantitative. Evaporation of the ethereal solution in vacuum over H_2SO_4 and KOH yields a red mass which loses its solubility in ether after standing for a few

days. The product is recrystallized from 50°C water, in which it dissolves very readily, except for a small yellow residue. On cooling, small red scales separate; these are again recrystallized from water.

SYNONYM:

Reinecke acid.

PROPERTIES:

Lustrous red leaflets; readily soluble in water, alcohol and acetone. Heating for several days at 70°C renders the acid anhydrous; further heating at 110–115°C imparts a darker color. The undried compound decomposes between 80 and 90°C, puffing up and evolving water.

REFERENCE:

R. Escales and H. Ehrensperger. Ber. dtsch. chem. Ges. 36, 2681 (1903).

Ammonium Tetrathiocyanatodianilinochromate (III)

$$NH_4[Cr(SCN)_4(C_6H_5NH_2)_2] \cdot 1^1/_2\,H_2O$$

a)
$$\underset{(\cdot 12\,H_2O)\ 499.4}{KCr(SO_4)_2} + 6\,KSCN = \underset{583.0}{K_3[Cr(SCN)_6]} + 2\,K_2SO_4$$

$$\underset{517.8}{K_3[Cr(SCN)_6]} + 4\,\underset{372.5}{C_6H_5NH_2} + \underset{60.1}{CH_3COOH} = \underset{657.8}{(C_6H_5NH_2)_2H[Cr(SCN)_4(C_6H_5NH_2)_2]} + 2\,KSCN + CH_3COOK$$

b)
$$\underset{657.8}{(C_6H_5NH_2)_2H[Cr(SCN)_4(C_6H_5NH_2)_2]} + \underset{17.0}{NH_3} = \underset{488.6}{NH_4[Cr(SCN)_4(C_6H_5NH_2)_2]} + 2\,\underset{186.2}{C_6H_5NH_2}$$

a) A mixture of 500 g. of chrome alum, 600 g. of *KSCN*, and 500 ml. of water is heated for 4 hours on a steam bath. The solution is cooled, 500 ml. of aniline is added, and the mixture is stirred for 3 hours at 60°C on a water bath. It is then again cooled and a mixture of 6 liters of water and 600 ml. of glacial acetic acid is added. After a few hours the precipitate is filtered and dissolved

in 1,5-2 liters of cold methanol. This solution is filtered, and 6 liters of water is added, whereupon $(C_6H_5NH_2)_2H[Cr(SCN)_4 \cdot (C_6H_5NH_2)_2]$ precipitates as a thick, violet crystal slurry. After 6 further precipitation from methanol-water, the yield is 330 g.
b) Four hundred grams of this anomalous anilinium salt is treated with 600 ml. of methanol and 300 ml. of conc. ammonia. This solution is cooled in ice and 3 liters of water is slowly added; the crude ammonium thiocyanoto-aniline complex precipitates. After filtering with suction, it is treated once more in the same manner with methanol, ammonia and water. Yield: about 200 g.

USE:

Separation of amino acids, especially proline.

SYNONYMS:

Ammonium salt of rhodanilic acid; ammonium rhodanilate.

PROPERTIES:

Violet-red crystals, somewhat soluble in water, very soluble in methanol, acetone and ethyl acetate. The solutions decompose on boiling. Insoluble in ether, benzene and chloroform.

DropBooks

REFERENCE:

M. Bergmann. J. Biol. Chem. 110, 476 (1935).

Potassium Tetrathiocyanatodipyridinochromate (III)

$$K[Cr(SCN)_4py_2] \cdot 2H_2O$$

Prepared from $K_3[Cr(SCN)_6]$ and pyridine.

Ten parts of $K_3[Cr(SCN)_6]$ (for preparation, see p. 1374), dried at 110°C, is heated with 30 parts of anhydrous pyridine in a small flask (4 hours on the water bath, in the absence of moisture). The hot solution is then poured into a crystallizing dish and allowed to chill in an ice chest. The solid which crystallizes is a mixture of KSCN, $py_2 \cdot H[Cr(SCN)_4py_2]$, and $[Kpy_4][Cr(SCN)_4py_2]$. It is suction-dried and placed on a clay plate. The complex potassium salt deliquesces over a period of 1-2 days, and the KSCN is extracted with water at room temperature, while the $K[Cr(SCN)_4py_2]$ is extracted with hot water. When cooled, the resulting red solutions gradually deposit small, lustrous red crystals of the potassium salt. The residue remaining after the hot water extraction affords pure dipyridinium salt $py_2 \cdot H[Cr(SCN)_4py_2]$.

PROPERTIES:

Formula weight 517.66. Small red crystals, which become anhydrous on heating to 110°C. Almost insoluble in cold water, but somewhat soluble in warm H_2O. Completely insoluble in benzene, chloroform and ether; very soluble in aqueous and absolute ethyl alcohol, methanol, ethyl acetate and pyridine; very readily soluble in acetone.

REFERENCE:

P. Pfeiffer. Ber. dtsch. chem. Ges. 39, 2121, 2123 (1906).

Trichlorotriaquochromium

$[CrCl_3(OH_2)_3]$

$$\underset{691.3}{3[CrCl_2(OH_2)_4]Cl} = \underset{424.9}{2[CrCl_3(OH_2)_3]} + \underset{266.5}{[CrCl_2(OH_2)_4]Cl \cdot 2\,H_2O}$$

Green chromium chloride hydrate $[CrCl_2(OH_2)_4]Cl \cdot 2\,H_2O$ is converted into $[CrCl_2(OH_2)_4]Cl$ on standing for 3 days in a vacuum desiccator over conc. H_2SO_4. It is then suspended in absolute ether; $[CrCl_3(OH_2)_3]$ is formed by disproportionation and dissolves with a brown-violet color. On evaporation of the ethereal solution in the absence of atmospheric moisture, $[CrCl_3(OH_2)_3]$ is obtained as an amorphous brown powder.

PROPERTIES:

Formula weight 212.43. Brown, amorphous, very hygroscopic powder, rapidly altered by traces of water. Soluble in water with a yellow-green color, which quickly becomes pure green owing to a reaction. Solutions in ether may be stored without change if moisture is absent.

REFERENCES:

A. Recoura. Comptes Rendus Hebd. Séances Acad. Sci. 194, 229 (1932); 196, 1854 (1933); see also F. Hein. J. prakt. Chem. 153, 168 (1939).

Trichlorotriethanolochromium

$[CrCl_3(C_2H_5OH)_3]$

$$\underset{158.4}{CrCl_3} + 3\,\underset{138.2}{C_2H_5OH} \rightleftharpoons \underset{296.6}{[CrCl_3(C_2H_5OH)_3]}$$

Dried $CrCl_3$ is refluxed (in the absence of moisture) with absolute alcohol and a small piece of zinc (or $CrCl_2$). The $CrCl_3$

dissolves; the solution, which is red when hot and green when cold, is concentrated in a vacuum desiccator over conc. H_2SO_4. The red crystals which deposit are washed with some absolute alcohol and ether, and stored dry.

PROPERTIES:

Dark red, hygroscopic crystals; soluble in alcohol, acetone and chloroform with a red color which soon becomes green. The aqueous solution decomposes rapidly.

REFERENCE:

I. Koppel. Z. anorg. Chem. 28, 471 (1901).

Trichlorotriamminechromium

$[CrCl_3(NH_3)_3]$

Prepared from $(NH_3)_3CrO_4$ and hydrochloric acid.

Five grams of triamminechromium tetroxide (for preparation, see p. 1392) is introduced into 50 ml. of well-cooled conc. HCl (constant stirring). The resulting gray- to blue-green precipitate is filtered off. The neutral complex, which deposits from the filtrate after standing for 1–2 days, is filtered with suction and washed with water until the washings become colorless. It is then dried by washing with alcohol and ether.

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PROPERTIES:

Formula weight 209.48. Blue crystals with greenish tinge, insoluble in cold H_2O. Dissolution in warm H_2O causes aquation to $[CrCl_2(OH_2)(NH_3)_3]Cl$. Presumably trans form.

REFERENCE:

A. Werner. Ber. dtsch. chem. Ges. 43, 2289 (1910).

Trichlorotripyridinechromium

$[CrCl_3py_3]$

I.

$$\underset{158.4}{CrCl_3} + 3\,py \underset{237.3}{} = \underset{395.7}{[CrCl_3py_3]}$$

The $CrCl_3$, in excess of dry pyridine, is refluxed in the presence of a small granule of $CrCl_2$. The $CrCl_3$ dissolves completely after

some time, giving a green color. The solution is filtered and cooled, whereupon the $[CrCl_3py_3]$ crystallizes out. On distilling the pyridine from the mother liquor, the compound can be obtained in almost quantitative yield.

II. Addition of H_2O to a pyridine solution of green chromium chloride hydrate $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$ yields a green powder which consists essentially of a mixture of $[CrCl_3py_3]$ and $[Cr(OH)_2(H_2O)_2py_2]Cl$. When this mixture is treated with HCl, the latter salt goes into solution as $[Cr(H_2O)_4py_2]Cl_3$, giving a deep red color. The residue consists of crude $[CrCl_3py_3]$. This is dissolved in conc. HCl and reprecipitated by pouring the filtered solution into a large amount of water. Finally the $[CrCl_3py_3]$ is recrystallized once more from pyridine.

PROPERTIES:

Green leaflets, readily soluble in pyridine, chloroform, acetone and conc. HCl; sparingly soluble in ethyl alcohol; insoluble in water, ether, benzene and naphtha.

REFERENCES:

P. Pfeiffer. Z. anorg. Chem. 24, 282 (1900); 55, 99 (1907).

Chromium (III) Glycinate

$(H_2NCH_2COO)_3Cr$

$$\underset{266.5}{CrCl_3 \cdot 6\,H_2O} + 3\,\underset{225.2}{H_2NCH_2COOH} + \underset{120.0}{3\,NaOH} = \underset{274.2}{(H_2NCH_2COO)_3Cr} + 3\,NaCl + 3\,H_2O$$

An aqueous solution of one mole of green chromium chloride hydrate and 3 moles of glycine is boiled while 3 moles of NaOH is added gradually. This gives a dark-red solution from which a violet compound separates. The latter is filtered off while the mixture is still hot. The filtrate, after cooling and standing in vacuum over H_2SO_4, deposits still more of the violet compound, together with larger red crystals. After suction-filtration and drying, the heavy red crystals are separated from the lighter violet ones by slurrying with alcohol. In this way, both compounds are obtained in analytically pure state.

PROPERTIES:

Red crystals = chromium (III) glycinate, $(H_2NCH_2COO)_3Cr$.

Violet crystals = so-called "basic" chromium (III) glycinate, $(NH_2CH_2COO)_2Cr(OH)_2Cr(OOCCH_2NH_2)_2 \cdot H_2O$.

Both compounds are sparingly soluble in water and insoluble in organic solvents.

Chromium (III) α-alaninate can be obtained in an analogous manner. If the reaction is allowed to take place in conc. solution, the red chromium (III) alaninate separates; the "basic" chromium (III) alaninate is obtained by evaporation of the solution.

REFERENCE:

H. Ley. Ber. dtsch. chem. Ges. 45, 380 (1912).

Chromium (III) Xanthate

$[(C_2H_5OCS_2)_3Cr]$

$$\underset{(\cdot 12\,H_2O)\ 499.4}{KCr(SO_4)_2} + 3\,\underset{480.9}{C_2H_5OCS_2K} = \underset{415.6}{[(C_2H_5OCS_2)_3Cr]} + 2\,K_2SO_4$$

A solution of 20 g. of potassium xanthate in some water is treated with a solution of 23 g. of chrome alum. The blue-black compound which precipitates is filtered off with suction and dried on a clay plate. It is dissolved in pyridine, and water is added in drops until a permanent clouding is obtained. The solution is then allowed to stand undisturbed to bring about crystallization. The crystals are separated by filtration and dried in vacuum.

PROPERTIES:

Dark-blue crystalline powder, soluble in organic media, insoluble in water.

REFERENCE:

J. V. Dubsky. J. prakt. Chem. 90, 118 (1914).

Chromium (III) Acetylacetonate

$(C_5H_7O_2)_3Cr$

$$\underset{(\cdot 6\,H_2O)\ 397.2}{Cr(CH_3COO)_3} + 3\,\underset{300.3}{C_5H_8O_2} = \underset{349.3}{[(C_5H_7O_2)_3Cr]} + 3\,CH_3COOH$$

A mixture of 40 g. of $[Cr(OH_2)_6](CH_3COO)_3$ (for preparation see p. 1371), 150 ml. of water, 40 g. of acetylacetone and 50 ml. of

2 N acetic acid is heated until solution is complete and crystallization of the internal complex begins. Then the solution is boiled for a short time until the liquid bumps vigorously. It is cooled gradually, then chilled in ice and filtered. The first crop affords 18 g. of chromium acetylacetonate, which can be recrystallized from chloroform-benzene.

II. $\underset{(9\,H_2O)\ 400.2}{Cr(NO_3)_3} + 3\,C_5H_8O_2 = [(C_5H_7O_2)_3Cr] + 3\,HNO_3$
$\qquad\qquad\qquad\qquad 300.3 \qquad\qquad 349.3$

An alcoholic solution of $[Cr(OH_2)_6](NO_3)_3$ is treated with the stoichiometric quantity of acetylacetone and then gently refluxed. The chromium complex crystallizes out after the excess alcohol is distilled off.

REFERENCES:

Red-violet crystals, m.p. 216°; can be sublimed in vacuum. Soluble in alcohol, chloroform and benzene; virtually insoluble in water and petroleum ether.

REFERENCES:

F. Hein. J. prakt. Chem. 153, 169 (1939); F. Gach. Monatsh. Chem. 21, 108 (1900).—As far as preparation from chromium chloride hexahydrate and acetylacetone in the presence of urea is concerned, see W. C. Fernelius and F. E. Blanch in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 130.

Chromyl Chloride

CrO_2Cl_2

I. $K_2CrO_4 + 2\,NaCl + 2\,H_2SO_4 = CrO_2Cl_2 + Na_2SO_4 + K_2SO_4 + 2\,H_2O$
$\qquad 194.2 \qquad 116.9 \qquad 196.2 \qquad 154.9$

A clay crucible is used to fuse 200 g. of K_2CrO_4 with 122 g. of NaCl at a temperature which should not be excessive. The melt is poured onto a sheet of iron and broken up into coarse pieces. These are placed in a 2-liter ground-joint flask and covered with 200 ml. of 100% H_2SO_4. A distilling condenser is connected to the flask at once, and a ground-joint receiving flask with a gas outlet tube is attached to the lower end of that condenser. When the initially vigorous reaction becomes moderate, the reaction flask is

heated gently until no further CrO_2Cl_2 distills. The crude product is purified by a second distillation in a dry ground-glass apparatus; the pure CrO_2Cl_2 is collected in dry glass ampoules, which are then melt-sealed.

II. $$\underset{294.2}{K_2Cr_2O_7} + 4\,\underset{116.9}{NaCl} + 3\,\underset{294.2}{H_2SO_4} = 2\,\underset{309.8}{CrO_2Cl_2} + K_2SO_4 + 2Na_2SO_4 + 3\,H_2O$$

It is possible to omit the fusion step. Thus, 150 g. of fuming H_2SO_4 is added in portions to a mixture of 50 g. of NaCl and 80 g. of $K_2Cr_2O_7$ (both thoroughly dried). Further procedure is the same as in method I. The yield is approximately 50%, based on $K_2Cr_2O_7$.

III. $$\underset{100.0}{CrO_3} + \underset{72.9}{2\,HCl} = \underset{154.9}{CrO_2Cl_2} + H_2O$$

A solution of 50 g. of CrO_3 in 170 ml. of conc. HCl is prepared, and 100 ml. of conc. H_2SO_4 is added in 20-ml. portions while cooling the flask in ice. The fluid mixture is poured into a separatory funnel, and after 20 minutes the lower CrO_2Cl_2 layer is drained into a small ground-joint flask. Dry air is bubbled through it for several minutes and the crude CrO_2Cl_2 is distilled as in method I.

DropBooks

PROPERTIES:

Deep-red liquid; fumes copiously in moist air. Should be stored in the dark and in sealed glass containers. M.p. −96.5°C, b.p. 117°C; d^{25}_4 1.9118. Can react explosively with combustible organic and inorganic substances. Soluble in other inorganic acid chlorides and organic liquids, such as $POCl_3$, CCl_4, $CHCl_3$ and C_6H_6.

REFERENCES:

I and III. L. Vanino. Handb. d. Präp. Chemie [Handbook of Preparative Chemistry], I, Stuttgart, 1925; p. 713.
II. E. Moles and L. Gomez. Z. phys. Chem. 80, 513 (1912).
See also H. H. Sisler, Inorg. Syntheses, Vol. II, New York–London, 1946, p. 205.

Chromium Trioxide-Pyridine

$$CrO_3 \cdot 2py$$

$$2\,C_5H_5N + CrO_3 = 2\,C_5H_5N \cdot CrO_3$$

Four grams of CrO_3 (0.04 mole) is dried in vacuum for four hours at 110°C and then chilled in ice-salt mixture. Fifty ml. of

pyridine (0.63 mole) is similarly chilled in a 300-ml. Erlenmeyer flask. The pyridine flask is agitated vigorously while situated in a cold bath, and the CrO_3 is slowly added. The flask is then stoppered and shaken further until solution is complete (solution is hastened by the use of a large excess of pyridine). The cooling is necessary to prevent oxidation of the pyridine. The excess solvent is then removed in vacuum. The product is sensitive to light. Slow evaporation favors the formation of large crystals. Yield: 10.3 g. (100%).

PROPERTIES:

Yellow to dark-red crystals. Soluble in pyridine; insoluble in CCl_4, benzene and ether. Hygroscopic. Decomposes slowly at 100°C; at higher temperatures, burns to give voluminous green chromium oxide. Hydrolyzes at once with water. Stable indefinitely in the dark. Stored in sealed containers at room temperature.

REFERENCES:

H. H. Sisler, J. D. Bush and O. E. Accountius, J. Amer. Chem. Soc. 70, 3827 (1948); O. E. Accountius, J. D. Bush and H. H. Sisler in: J. C. Bailar, Inorg. Syntheses, Vol. IV, New York-London-Toronto, 1953, p. 94.

Chromyl Nitrate

$$CrO_2(NO_3)_2$$

$$\underset{100.0}{CrO_3} + \underset{108.0}{N_2O_5} = \underset{208.0}{CrO_2(NO_3)_2}$$

A powder funnel is used to rapidly pour 8.3 g. of N_2O_5 into a 50-ml. ground-joint flask precharged with 7 g. of CrO_3 and a few (vacuum) boiling stones. The flask is attached to a distillation apparatus whose joints are lubricated with silicone grease and which is protected against entry of atmospheric moisture by means of a P_2O_5 tube. The reaction begins after a short time, with fusion of the solids. The reaction mixture should be left standing overnight at room temperature.

The dark-red liquid product is distilled in aspirator vacuum. A liquid-nitrogen-cooled trap is interposed between the apparatus and the aspirator to prevent access of moisture and to condense the NO_2 and N_2O_5 which distill off. The $CrO_2(NO_3)_2$ distills at a bath temperature of about 75°C (partial decomposition). The receiver then contains 5.8 g. of pure $CrO_2(NO_3)_2$.

PROPERTIES:

Dark-red liquid, sensitive to moisture. M.p. −27°C, b.p. (10^{-3} mm.) 28°C; (17 mm.) 67°C. Decomposes at about 120°C.

REFERENCES:

M. Schmeisser and D. Lützow, Angew. Chem. 66, 230 (1954); D. Lützow, Thesis, Univ. München, 1955.

Chromyl Perchlorate

$CrO_2(ClO_4)_2$

$$\underset{100.0}{CrO_3} + 2\,\underset{333.8}{Cl_2O_7} = \underset{282.9}{CrO_2(ClO_4)_2} + 2\,\underset{134.9}{ClO_4} + {}^1/_2O_2$$

A two-neck flask is used; then, at −50°C, 5 g. of Cl_2O_6, followed by 3 g. of CrO_3, is added through one neck. This neck is then closed off either with a ground stopper lubricated with fluorinated hydrocarbon grease (see under Cl_2O, p. 299 f.), or by sealing off. The other neck leads to a manifold carrying sealable ampoules and a second, similar flask. The open end of the manifold is closed off with a P_2O_5 tube.

The cold bath is now replaced with a bath at +6°C. The Cl_2O_6 melts, and the two components react vigorously. The reactor is allowed to stand at 0°C for several hours (preferably overnight). After this, no further gases are evolved.

The reactor is now cooled with liquid nitrogen and the entire system evacuated to about 0.1 mm. The cold bath is removed and the second flask (at the manifold) is cooled; within a few minutes, Cl_2 and ClO_2 distill with foaming. To remove these gases completely, the vessel is immersed in a bath at +20°C for one half hour and vacuum is applied. As soon as no further volatiles distill, the bath temperature is raised to about 35–36°C. The $CrO_2(ClO_4)_2$ now distills into the manifold and flows into the first ampoule (transparent red liquid). The manifold with the ampoules should be somewhat inclined. When sufficient compound has collected in the first ampoule, the latter is sealed off. Additional distilled product collects in the stub left from the first ampoule, and is driven into the next ampoule by heating with a hot-air blower.

PROPERTIES:

Red liquid, very sensitive to moisture. M.p. −1°C, b.p. (extrapolated) (760 mm.) 174.7°C; (0.08 mm.) 35°C; (0.8 mm.) 45°C. Powerful oxidant; dissolves in CCl_4. May be stored for months in the dark at Dry Ice temperature. Often explodes at +80°C.

Library Books

REFERENCES:

M. Schmeisser. Angew. Chem. 67, 493 (1955); D. Lützow. Thesis, Univ. München, 1955.

Rubidium Chromate

Rb_2CrO_4

I. $$\underset{231.0}{Rb_2CO_3} + \underset{100.0}{CrO_3} = \underset{287.0}{Rb_2CrO_4} + CO_2$$

Obtained by evaporation of an aqueous solution of CrO_3 which has been neutralized with Rb_2CO_3 (or RbOH).

The by-product $Rb_2Cr_2O_7$ forms at even a very small excess of CrO_3; therefore somewhat more than the stoichiometric quantity of Rb_2CO_3 should be used.

II. Preparation analogous to that of Cs_2CrO_4.

PROPERTIES:

Yellow, rhombic crystals, isomorphous with K_2CrO_4 and K_2SO_4. Readily soluble in water (42% at 20°C).

REFERENCES:

L. Grandeau. Ann. Chim. Phys. (3) 67, 228 (1863); J. W. Retgers. Z. phys. Chem. 8, 39 (1891); Abeggs Handbuch der anorg. Chemie [Abegg's Handbook of Inorganic Chemistry], IV, 1, p. 362 (1921).

Rubidium Dichromate

$Rb_2Cr_2O_7$

I. $$\underset{231.0}{Rb_2CO_3} + 2\,\underset{200.0}{CrO_3} = \underset{387.0}{Rb_2Cr_2O_7} + CO_2$$

Obtained by evaporation of stoichiometric mixtures of Rb_2CO_3 (or RbOH) and CrO_3.

II. Preparation analogous to that of $Cs_2Cr_2O_7$.

PROPERTIES:

Trimorphic; forms A and B deposit together from solution above 35°C. Orange-colored monoclinic or red triclinic crystals. Moderately soluble in water (5% at 18°C).

REFERENCES:

L. Grandeau. Ann. Chim. Phys. (3), 67, 227 (1863); Abegg Handbuch der anorg. Chemie IV, 1, p. 362 (1921).

Cesium Chromate

Cs_2CrO_4

$$\underset{481.8}{Cs_2Cr_2O_7} + \underset{171.4}{Ba(OH)_2} = \underset{253.4}{BaCrO_4} + \underset{384.9}{Cs_2CrO_4} + H_2O$$

A small excess of $Ba(OH)_2$ is added to a warm solution of $Cs_2Cr_2O_7$. The sparingly soluble $BaCrO_4$ is filtered off and the solution is concentrated until crystallization occurs.

PROPERTIES:

Yellow hexagonal or rhombic crystals, readily soluble in water.

DropBooks

REFERENCE:

J. H. de Boer, J. Broos and H. Emmens. Z. anorg. allg. Chem, 191, 113 (1930).

Cesium Dichromate

$Cs_2Cr_2O_7$

$$\underset{252.1}{(NH_4)_2Cr_2O_7} + \underset{336.7}{2\,CsCl} = \underset{481.8}{Cs_2Cr_2O_7} + 2\,NH_4Cl$$

Reaction of warm solutions of $(NH_4)_2Cr_2O_7$ and CsCl, followed by cooling, yields orange-red crystals of $Cs_2Cr_2O_7$, which are often contaminated with about 5% of $(NH_4)_2Cr_2O_7$. To decompose the ammonium salt, the product is calcined at a low temperature. Recrystallization gives an excellent yield of pure $Cs_2Cr_2O_7$.

PROPERTIES:

Orange-red triclinic crystals; sparingly soluble in cold, readily soluble in hot water.

REFERENCE:

J. H. de Boer, J. Broos and H. Emmens. Z. anorg. allg. Chem. 191, 113 (1930).

Potassium Fluorochromate

$K[CrO_3F]$

$$\underset{294.2}{K_2Cr_2O_7} + 2\,\underset{40.0}{HF} = 2\,\underset{316.2}{K[CrO_3F]} + H_2O$$

Powdered $K_2Cr_2O_7$ is heated in a Pt dish with excess of conc. HF until solution is complete. On cooling, $K[CrO_3F]$ separates as red crystals.

PROPERTIES:

Formula weight 158.11. Ruby-red bipyramids, readily soluble in water. Etches glass vessels in which it is stored. Crystal structure: tetragonal (space group C_{4h}^6).

REFERENCES:

A. Streng. Liebigs Ann. 129, 227 (1864); J. A. A. Ketelaar and E. Wegerif. Recueil Trav. Chim. Pays-Bas 57, 1269 (1938).

Potassium Chlorochromate

$K[CrO_3Cl]$

$$\underset{294.2}{K_2Cr_2O_7} + 2\,\underset{72.9}{HCl} = 2\,\underset{349.1}{K[CrO_3Cl]} + H_2O$$

I. Fifty grams of fine $K_2Cr_2O_7$ powder is dissolved in a mixture of 65 ml. of conc. HCl and 50 ml. of water (by heating to 70°C). The solution is filtered through a jacketed funnel heated with hot water. After 1–2 days, the nascent crystals are filtered off with suction, recrystallized from glacial acetic acid, and dried in a vacuum desiccator over H_2SO_4.

II.
$$\underset{194.2}{K_2CrO_4} + \underset{154.9}{CrO_2Cl_2} = 2\,\underset{349.1}{K[CrO_3Cl]}$$

A three-neck flask is fitted with a stirrer, a thermometer, a dropping funnel, and a gas outlet tube. A solution of 75 g. of

K_2CrO_4 in 125 ml. of hot water is placed in the flask, and 86 g. of CrO_2Cl_2 is added dropwise with stirring. The temperature is held at 90–100°C by means of a Bunsen burner. Stirring is continued for 1 hour at the same temperature and the flask contents are then poured into a beaker. After 18 hours the nascent crystals are filtered off with suction and pressed together firmly to remove the mother liquor as thoroughly as possible without washing. The product is then placed on a clay plate, covered with a watch glass, and allowed to stand for 10 hours. Yield: 109 g. (81%, based on K_2CrO_4).

The mother liquor, cooled at 0°C for 1.5 hours, yields about 16 g. of less pure $K[CrO_3Cl]$. To purify this, 30 g. of the impure product is dissolved in 100 ml. of acetone, filtered, and 700–800 ml. of CCl_4 is added slowly with stirring; 16–17 g. of pure $K[CrO_3Cl]$ is thus obtained.

PROPERTIES:

Formula weight 174.56; d 2.497. Sparkling, orange-colored crystalline needles, soluble in glacial acetic acid and acetone. Undergoes hydrolytic cleavage in water. Heating the salt to 100°C causes loss of chlorine.

DropBooks

REFERENCES:

I. L. Vanino, Handb. d. Präp. Chemie [Handbook of Preparative Chemistry], I, Stuttgart, 925, p. 321.
II. H. H. Sisler in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York–London, 1946, p. 208.

Potassium Tetraperoxochromate (V)

K_3CrO_8

Prepared from KOH, CrO_3 and H_2O_2.

A mixture of 25 ml. of 50% CrO_3 solution, 100 ml. of 25% KOH, and 100 ml. of H_2O is cooled in a cold bath until ice begins to form. Now, 30 ml. of 30% H_2O_2 is added dropwise (with shaking), care being taken to keep the solution temperature from rising above 0°C. The initially red-yellow solution soon acquires a black-brown color. The salt which drops to the bottom of the vessel after 1–2 hours is filtered off with suction, washed with 95% alcohol until the washings are colorless, then with ether, and stored in a stoppered vessel. The yield is about 50%, based on the H_2O_2 used.

PROPERTIES:

Formula weight 297.30. Red-brown crystals, which may be stored for months without decomposition. Moderately soluble in cold water, insoluble in alcohol and ether.

REFERENCE:

E. H. Riesenfeld, H. E. Wohlers and W. A. Kutsch. Ber. dtsch. chem. Ges. 38, 1887 (1905).

Ammonium Pentaperoxodichromate

$(NH_4)_3Cr_2O_{12} \cdot 2\,H_2O$

Prepared from NH_4Cl, CrO_3 and H_2O_2.

The procedure for the blue ammonium salt is the same as that used for K_3CrO_8 (see above). The quantities used are: 100 ml. of H_2O, 5 ml. of conc. HCl, 10 g. of NH_4Cl, 10 ml. of 50% CrO_3 solution, and 25 ml. of 30% H_2O_2. At the end, the product is washed only briefly with 90% alcohol.

PROPERTIES:

Formula weight 386.13. Violet-black crystalline powder consisting of flat prisms which show strong pleochroism (bright red-brown and dark blue-violet). May be stored for a few days in a cold desiccator; transforms completely to $(NH_4)_2CrO_4$ on 24-hour exposure in the air; decomposes explosively at 50°C to Cr_2O_3. Soluble in ice water (violet-brown color).

REFERENCES:

E. H. Riesenfeld, H. E. Wohlers and W. A. Kutsch. Ber. dtsch. chem. Ges. 38, 1888 (1905); O. F. Wiede. Ber. dtsch. chem. Ges. 31, 518 (1898); R. Schwarz and H. Giese. Ber. dtsch. chem. Ges. 66, 310 (1933).

Diperoxotriamminechromium (IV)

$(NH_4)_3CrO_4$

Prepared from ammonia, CrO_3 and H_2O_2.

A mixture of 25 ml. of 10% ammonia and 5 ml. of 50% CrO_3 solution is treated dropwise at 0°C with 5 ml. of 30% H_2O_2. The

resultant solution is first allowed to stand for one hour in a cooling mixture, and is then heated (together with the copious precipitate of $(NH_4)_2Cr_2O_7$ contained therein) to about 50°C until the vigorous evolution of gas ceases and the salt dissolves almost completely. Finally, the solution is filtered and cooled once more to 0°C. The $(NH_3)_3CrO_4$ which crystallizes is filtered off with suction, washed with absolute alcohol and ether, and dried in a desiccator over KOH. Yield: about 0.3 g.

SYNONYMS:

Chromium tetroxide triammine or triamminechromium tetroxide.

PROPERTIES:

Formula weight 167.11; $d^{16.8}$ 1.964. Light-brown needles, soluble in dilute ammonia and water (partial decomposition). Insoluble in other solvents. The product should be protected from moisture, but because of the danger of explosion, storage ampoules other than the type sealed by fusion of the outlet should be used.

REFERENCES:

DropBooks

E. H. Riesenfeld. Ber. dtsch. chem. Ges. 38, 4070 (1905); O. F. Wiede. Ber. dtsch. chem. Ges. 30, 2180 (1897); for discussion of valence state, see S. S. Bhatnagar, B. Prakash and A. Hamid. J. Chem. Soc. (London) 1938, 1432.

Barium Orthochromate (IV)

Ba_3CrO_5

$$\underset{253.4}{BaCrO_4} + \underset{152.0}{Cr_2O_3} + 5\,\underset{858.9}{Ba(OH)_2} = 3\,\underset{1172.2}{Ba_3CrO_5} + 5\,H_2O$$

Stoichiometric quantities of the starting materials, which must be very pure and anhydrous, are thoroughly mixed. (However, a very small excess of $Ba(OH)_2$, i.e., 0.03–0.06 moles BaO/atom Cr, must be provided. Any larger excess of the base will give rise, in the heating which follows, to partial or sometimes complete formation of tribarium chromate (IV), Ba_3CrO_5. The latter is a heavy, blackish-green, glittering crystalline powder which appears olive-brown under the microscope.)

About 4 g. of the mixture is then heated in a sintered alumina boat in an O_2-free nitrogen stream (2 hours at 900–950°C).

PROPERTIES:

Microcrystalline, heavy emerald green powder. Readily soluble in dilute HCl or $HClO_4$, even in the cold, with brownish yellow color. Water causes hydrolysis. Stable to methanol.

REFERENCE:

R. Scholder and G. Sperka. Z. anorg. allg. Chem. 285, 49 (1956).

Barium Chromate (V)

$Ba_3(CrO_4)_2$

$$\underset{506.7}{2\,BaCrO_4} + \underset{197.4}{BaCO_3} = \underset{644.1}{Ba_3(CrO_4)_2} + CO_2 + {}^1/_2\,O_2$$

An intimate mixture of 1 mole of $BaCrO_4$ and 0.50 moles of $BaCO_3$ is heated in an O_2-free nitrogen stream at 1000°C. Four hours of heating suffices for about 2 g. of reactants. The $Ba_3(CrO_4)_2$ product is of excellent purity.

PROPERTIES:

Black-green microcrystalline powder. Water causes gradual decomposition. Completely soluble in dilute acids, with disproportionation to Cr (III) and Cr (VI).

REFERENCE:

R. Scholder and W. Klemm. Angew. Chem. 66, 463 (1954).

Sodium Thiochromite

$NaCrS_2$

Prepared by reaction of K_2CrO_4 with a soda-sulfur melt.

An intimate mixture of 1 part of K_2CrO_4 with 30 parts of $KNaCO_3$ and 30 parts of sulfur is heated for 30-60 minutes in a covered sintered alumina crucible; the latter is placed in an electric furnace. The temperature is 750-850°C. After heating, the crucible is allowed to cool slowly. The cold melt is slurried in water, then washed by decantation several times with dilute NaOH. The thiochromite is filtered off and thoroughly washed, first with dilute alcoholic NaOH, then with pure alcohol, and finally with ether. The product is free of potassium despite the use of K salts.

PROPERTIES:

Formula weight 139.13; d 3.2. Crystalline gray-black aggregate with a greenish luster. Well-formed hexagonal leaflets are produced above 800°C; these appear garnet-red by transmitted light. When moist, rapidly darkens and decomposes on exposure to air.

REFERENCES:

W. Rüdorff and K. Stegemann. Z. anorg. allg. Chem. 251, 379 (1943); R. Schneider. J. prakt. Chem. 56, 415 (1897).

Dibenzenechromium (0)

$(C_6H_6)_2Cr$

$$\underset{475.1}{3\,CrCl_3} + \underset{53.9}{2\,Al} + \underset{133.3}{AlCl_3} + \underset{466.6}{6\,C_6H_6} \xrightarrow{AlCl_3} 3\,[Cr(C_6H_6)_2][AlCl_4]$$

$$2\,[Cr(C_6H_6)_2]^+ + S_2O_4^{2-} + 4\,OH^- \rightarrow \underset{416.5}{2\,Cr(C_6H_6)_2} + 2\,SO_3^{2-} + 2\,H_2O$$

DropBooks

A 250-ml. three-neck flask is used, and 25 g. (0.16 moles) of anhydrous $CrCl_3$, 3.5 g. (0.13 moles) of dry Al powder, and 60 g. (0.45 moles) of sublimed and rapidly ground $AlCl_3$ are weighed in. The flask is evacuated several times with an aspirator and refilled with dry, O_2-free nitrogen. Then, 150 ml. of absolute benzene is introduced in a countercurrent stream of inert gas. The flask is again evacuated for several minutes to remove traces of HCl (with the evaporating benzene). Then, 10 drops (0.3 ml.) of mesitylene are added under protection of the N_2 blanket. The flask is now fitted with a reflux condenser carrying a mercury pressure-relief valve. A high-speed Hg-seal stirrer and a stopper are placed on the other necks.

The N_2 stream is cut off and the mixture is refluxed for 35–40 hours with vigorous stirring. The flask contents are cooled, then decomposed by pouring slowly (under N_2) into 200 ml. of CH_3OH contained in a 4-liter three-neck flask. The latter is cooled in ice; two of the necks are fitted with stopcocks and the third carries a high-speed Hg-seal stirrer. Then 200 ml. of H_2O is also added. When hydrolysis is complete, 2 liters of benzene is added, then a solution of 220 g. of KOH in 500 ml. of H_2O. Finally, 220 g. of solid sodium dithionite is rapidly introduced. After 2 hours of high-speed stirring, the dark-brown solution is carefully filtered with suction (in the absence of air) into an evacuated 3-liter flask,

which carries an N_2 inlet tube. The solution is dried with solid KOH. It is then transferred (under N_2) to a distillation apparatus, and the solvent is removed thoroughly on a hot water bath. The solid black residue is washed 3 times with absolute ether (under N_2) and then sublimed in high vacuum at 160°C. Yield: 29.5 g. (90% of theoretical).

PROPERTIES:

Black, diamagnetic crystals, sensitive to air. M.p. 284–285°C. Slightly soluble in ether and petroleum ether, giving a brown color; moderately soluble in benzene.

REFERENCES:

E. O. Fischer and W. Hafner. Z. Naturforsch. 10b, 665 (1955); Z. anorg. allg. Chem. 286, 146 (1956); E. O. Fischer, W. Hafner and J. Seeholzer. Private communication.

Bis(diphenyl)chromium (0)

$(C_{12}H_{10})_2Cr$

$$[(C_{12}H_{10})_2Cr]^+ \xrightarrow{S_2O_4^{2-}} (C_{12}H_{10})_2Cr$$

The melt is prepared and hydrolyzed in the same manner as described below for bis(diphenyl)chromium (I) iodide. The first filtrate is rejected.

An excess of alkaline sodium dithionite solution is added under N_2 to the later, pure orange-red filtrates, whereupon the bis(diphenyl)chromium (I) cation is reduced instantly and precipitates as bis(diphenyl)chromium (0). After standing for one half hour the precipitate is filtered off on a large, fine fritted-glass funnel and then dried for 1–2 days over P_2O_5. It is then extracted with ether or pentane in the absence of air; the bis(diphenyl)chromium separates from the solvent in beautiful small crystals. These are filtered off, dried in vacuum, and stored under N_2. Yield: 10 to 12 g.

PROPERTIES:

Crystals with brasslike luster, M.p. (not sharp) at 112°C. Soluble in ether, alcohol, benzene, etc.; diamagnetic. Limited stability in air when dry. Dibenzenechromium (0) and diphenylbenzenechromium (0) can be prepared from the corresponding chromium (I) salts in esentially the same way.

REFERENCES:

E. O. Fischer and D. Seus. Chem. Ber. 89, 1814 (1956); F. Hein and W. Kleinwächter. Private unpublished communication.

Dibenzenechromium (I) Iodide

$[(C_6H_6)_2Cr]I$

Ten grams (0.05 moles) of $Cr(C_6H_6)_2$ fine powder is shaken with 200 ml. of benzene and 100 ml. of H_2O in a separatory funnel, while air is passed through, until all the solid dissolves and the benzene phase becomes virtually colorless. The yellow-brown aqueous layer is filtered and treated with saturated aqueous KI solution (stirring) until no further yellow precipitate separates out. After cooling in ice, the precipitate is filtered off, washed 3 times with some C_2H_5OH, and finally with ether. It is then dried in vacuum. Yield: 10.5 g., or 65% based on $Cr(C_6H_6)_2$.

PROPERTIES:

Egg-yellow, stable in air, moderately soluble in H_2O.

DropBooks

REFERENCES:

E. O. Fischer and W. Hafner. Z. anorg. allg. Chem. 286, 146 (1956); E. O. Fischer. Private communication.

Bis(diphenyl)chromium (I) Iodide

$[Cr(C_{12}H_{10})_2]I$

Ten grams of sieved, anhydrous $CrCl_3$ dust, 8 g. of Al powder, 27 g. of sublimed diphenyl, and 30 g. of $AlCl_3$ (powdered in a mortar) are separately dried for one half hour in an oven at 110°C. Then, the $CrCl_3$ is mixed intimately with the Al powder, and the biphenyl with the $AlCl_3$. The two mixtures are then blended thoroughly with each other in a 150-ml. beaker placed in a drying oven. Finally, the total mixture is covered with a layer of pure biphenyl (3–4 g.), and the beaker is covered with a watch glass. The beaker is now placed in a silicone oil bath preheated to 100°C, and the bath temperature is slowly raised to 110°C. As soon as the reaction begins (110–120°C, melting of the mass, followed by puffing up and evolution of HCl vapors), the heating of the oil bath is discontinued. The heat of reaction causes the

temperature of the mixture to rise spontaneously to 140–150°C. After 10 minutes the melt is stirred vigorously with a thermometer, care being taken to keep the temperature from rising above 160°C. The reaction is allowed to complete itself in one half hour. During this time, the oil bath temperature is kept at 120°C. Careful conduct of the melt reaction is most important in this preparation.

The beaker with the melt is now cooled to room temperature. The melt is added with a spatula to 100 ml. of methanol (addition in portions) in an 800-ml. beaker placed in an ice bath. An orange-red to brown solution forms; cold, saturated NaCl solution is then added with stirring. This yields an easily filtered product which is separated once on a 15-cm. Buchner funnel. Then about 3 g. of solid KI is added to the acidic, dark-brown filtrate: this causes precipitation of the bis(diphenyl)chromium (I) cation present. However, most of the product is in the filtration residue, and is obtained by leaching the residue several times (on the funnel) with 100-ml. portions of water, followed by suction-drying. Before each leaching, a fast stream of air is drawn through the filter cake for 10–15 minutes, in order to oxidize any remaining chromium (0) to the monovalent state. The leaching is discontinued when the wash water becomes almost colorless. The bis(diphenyl)chromium (I) iodide is reprecipitated by stirring about 8–10 g. of solid KI into the filtrate. It is filtered off with suction and washed with water, then 10 ml. of alcohol and two 10-ml. portions of ether. Yield: 22–25 g. The crude product is already very pure; it can be recrystallized from alcohol.

PROPERTIES:

Formula weight 487.33; m.p. 157°C. Depending on size, orange to reddish black crystals. Soluble in pyridine, alcohol, chloroform, acetone; almost insoluble in benzene and water; insoluble in ether and naphtha. Not sensitive to dilute hydrochloric acid.

REFERENCES:

F. Hein. Ber. dtsch. chem. Ges. 54, 2716 (1921); E. O. Fischer and D. Seus. Chem. Ber. 89, 1814 (1956); F. Hein and W. Kleinwächter. Unpublished private communication.

(Diphenyl)(benzene)chromium (I) iodide

$$[(C_{12}H_{10})Cr(C_6H_6)]I$$

All operations are conducted under pure N_2 in the absence of moisture.

A Grignard solution is prepared from 37 g. of magnesium, 236 g. of bromobenzene and 900 ml. of absolute ether. After the

end of the reaction, the solution is decanted from the unreacted Mg into a 1.5-liter sulfonation flask, which is provided with a stirrer, a thermometer, a tap-injection bulb from which solid reagents can be added, and inlet and outlet tubes for N_2.

The solution is cooled to −15 to −18°C. Vigorous stirring and good cooling are provided, and 40 g. of sublimed $CrCl_3$ is tapped from the bulb into the flask at a uniform rate; total addition time: 2 to 3 hours. (The $CrCl_3$ is preextracted with boiling HCl, washed, dried, and sieved through a U. S. standard 60-mesh screen.) The reaction temperature should not rise above −12°C. The mixture becomes black-brown. After the addition of $CrCl_3$, stirring is continued 2 to 3 hours. After standing overnight in an ice chest, the mixture is stirred thoroughly and decomposed by pouring it slowly onto an ice-H_2SO_4 mixture (750 g. of ice, 25 ml. of conc. H_2SO_4) contained in a 4-liter breaker. The addition proceeds in air and with constant stirring while the beaker is immersed in an ice-salt bath. The yellow-red ethereal emulsion is rapidly decanted into a dish and the ether is driven off. The aqueous layer is filtered through a suction funnel with the largest possible filtering surface.

The residue from the ethereal layer is stirred with approximately 50 ml. of 50% KI and 50 ml. of saturated Na_2SO_3 solution, and is then thoroughly extracted with chloroform (shaking in a separatory funnel) until the solvent is only slightly yellow. The aqueous solution, which contains KI, is combined with the filtrate from the aqueous layer and similarly extracted with chloroform. The residue from the filtration of the aqueous layer, the filter paper, the funnel, and all vessels are also extracted with chloroform. The combined orange-colored chloroform extracts (which contain the crude iodide) are washed twice, each time with 15 ml. of KI and 10 ml. of Na_2SO_3 solutions, then once with 25 ml. of H_2O, and dried for 24 hours over anhydrous potassium carbonate. The filtered chloroform solution is concentrated, under anhydrous conditions, in aspirator vacuum at a bath temperature of 25 to 30°C. The residual viscous mass is rinsed into a dish with a minimum amount of chloroform. To remove diphenyl, the material is triturated, first with 100-ml. portions and later with 30-ml. portions of absolute ether, until a sample of extract shows almost no residue on evaporation. A total of 1.5 to 2 liters of absolute ether is required. The viscous, red-orange, crude iodide hardens and becomes powdery as the extraction of diphenyl progresses. It is dried over P_2O_5 in vacuum. It may be kept for months if stored in a cool place away from light. Yield: 35–40 g. of crude iodide. It is composed of bis(diphenyl)chromium (I) iodide, (diphenyl)(benzene)chromium (I) iodide (the principal constituent), and a very small percentage of dibenzenechromium (I) iodide.

To obtain pure (diphenyl)(benzene)chromium (I) iodide, the procedure is as follows: 39 g. of crude iodide is dissolved in 900 ml. of methanol, treated with 300 ml. of water, and passed through an anion exchange column (e.g., OH form of Wofatit L 150 or Amberlite IRA 410; 150 g. of dry material in 70% methanol) at a rate of 3 ml./min. The column is then eluted with 70% alcohol and the yellow to orange fraction of the filtrate is collected in the absence of CO_2. This fraction is concentrated in aspirator vacuum at a bath temperature of 30–35°C until a methanol-free solution remains. This is filtered to remove a slight cloudiness (diphenyl). The clear, filtered solution is diluted to 300 ml. with water and treated with a solution of 18 g. of anthranilic acid (m.p. 145°C) and 12 g. of KOH in 60 ml. of H_2O while cooling the flask in ice; this treatment causes the $(C_{12}H_{10})_2Cr$ (I) anthranilate to deposit as an orange-yellow, amorphous precipitate. After standing for 3 hours, the precipitate is removed by filtration through a very fine fritted-glass funnel. The filtrate is treated with 20 g. of solid KI in a separatory funnel. The $(C_{12}H_{10})(C_6H_6)CrI$ separates at once as an oil. The oil is extracted with chloroform until the latter is only slightly yellow. The combined chloroform extracts are thoroughly shaken with some 20% KI solution, and then with a very small quantity of water; the extracts are then dried for several hours over potassium carbonate. The filtered solutions are concentrated by distilling off the chloroform in vacuum (under anhydrous conditions) at a bath temperature of 30–35°C. Finally, about a 10-fold quantity of absolute ether is added, causing an orange-red oil to separate; this gradually solidifies and can be ground under ether. The supernatant ether layer is replaced 2 or 3 times to remove the chloroform. The powder is filtered off under anhydrous conditions, washed several times with ether, and dried in a drying pistol at 2 mm. and 55–60°C (using acetone as the heating medium). The product is recrystallized by dissolving in absolute alcohol at 60–70°C (anhydrous conditions), filtering through a very fine fritted-glass funnel while still hot, and storing overnight at −20°C. This yields massive orange-red crystals. The $(C_{12}H_{10})(C_6H_6)CrI$ can also crystallize in golden-yellow hexagonal leaflets, but these transform into the orange-red crystals after standing for several days in the mother liquor.

Since the $(C_{12}H_{10})(C_6H_6)CrI$ often separates as an oil, seeding the solution may be helpful. The precipitation can be completed by very slow addition of a 3- to 5-fold quantity of ether. The precipitate is filtered off under anhydrous conditions, washed twice with some 1:1 absolute ether/absolute ethanol, twice with absolute ether, and then dried to a constant weight in a drying pistol at 2 mm. and 55–60°C (using acetone as the heating medium). This drying quantitatively removes the ether, which otherwise adheres tenaciously. Yield: 26 g. of $(C_{12}H_{10})(C_6H_6)CrI$.

The (diphenyl)(benzene)chromium (I) iodide can also be prepared by a reductive Friedel-Crafts reaction, starting with an appropriate mixture of benzene, diphenyl, $CrCl_3$, $AlCl_3$ and Al powder. The reaction can be carried out under reflux at atmospheric pressure, but again affords (dipheny)(benzene)chromium in a mixture with dibenzenechromium and bis(diphenyl)chromium. After conversion to the iodides, they must be separated from each other in a manner analogous to that given above.

The yield in this method, even under the most favorable conditions, is lower than that of the Grignard procedure.

PROPERTIES:

Formula weight 411.33. Red-orange, massive, somewhat light-sensitive crystals. M.p. approximately 160°C (decomp.). Can be stored in vacuum or under N_2 in the dark. Readily soluble in pyridine; soluble in chloroform, alcohol and acetone; less soluble in water; insoluble in ether, benzene and petroleum ether.

REFERENCES:

F. Hein. Ber. dtsch. chem. Ges. 54, 2741 (1921); F. Hein and H. Meininger. Z. anorg. allg. Chem. 145, 115 (1925); F. Hein and E. Markert. Ber. dtsch. chem. Ges. 61, 2261 (1928); F. Hein, P. Kleinert and E. Kurras. Z. anorg. allg. Chem. 289, 229 (1957); H. H. Zeiss and M. Tsutsui. J. Amer. Chem. Soc. 79, 3062 (1957); F. Hein and K. Eisfeld. Z. anorg. allg. Chem. 292, 162 (1957).

Molybdenum

Mo

I. $$\underset{144.0}{MoO_3} + 3\,\underset{67.3\,l.}{H_2} = \underset{96.0}{Mo} + 3\,\underset{54.1}{H_2O}$$

The MoO_3 is obtained by heating ammonium molybdate. Since MoO_3 is volatile at higher temperatures, it is prereduced in a stream of hydrogen at about 500°C to the nonvolatile lower oxides. The oxides are then reduced to the metal at about 1000°C. The product is allowed to cool in an H_2 stream, and the metal is obtained as a gray-black powder.

II. $$\underset{383.9}{3\,MoO_4} + \underset{107.9}{4\,Al} = \underset{287.9}{3\,Mo} + \underset{203.0}{2\,Al_2O_3}$$

Because of the volatility of MoO_3, the starting material is MoO_2, which is obtained by reduction of MoO_3 with H_2 at

dark-red heat. A clay crucible embedded in dry sand is used, and a mixture of 80 g. of MoO_2 and 21 g. of Al powder (or, better, Al granules the size of grains of sand) is placed in it. The mixture is caused to react by means of an ignition mixture.* After cooling the crucible is broken up, and the solid melt of MO, weighing about 50 g. (about 90% yield), is isolated. If 60 g. or 40 g. of MoO_2 is charged, the yield drops to 70-80%. The metal contains 98-98.5% Mo as well as some Si, Fe and Al.

PROPERTIES:

Solid Mo is bright, with a silvery luster. Powder is light- to black-gray, depending on particle size. M.p. 2620°C; d 10.23; hardness 5.5. Attacked (with difficulty) by nonoxidizing acids and aqueous alkalies. Crystal structure: A 2 type.

REFERENCES:

H. Funk. Darst. der Metalle im Laboratorium [Preparation of Metals in the Laboratory], Stuttgart, 1938, p. 69 f.; H. Biltz and R. Gärtner. Ber. dtsch. chem. Ges. 39, 3370 (1906).

Dibenzenemolybdenum (0)

$(C_6H_6)_2Mo$

An intimate mixture of 4 g. (0.015 moles) of $MoCl_5$, 3 g. (0.023 moles) of anhydrous fine $AlCl_3$ powder and 1 g. (0.04 g.-atoms) of Al powder is placed in a glass combustion tube of about 75-ml. capacity. About 30 ml. of absolute benzene is then added. The tube is evacuated, sealed, placed in an iron protective tube, and heated in a horizontal position for 15 hours at 120°C.

After cooling, the tube is carefully opened and the dark-colored contents are decomposed with 20 ml. of methanol (cooling) and then treated with 75 ml. of water. The residue is filtered off on a

*Ignition mixture (German "Zündgemisch" or "Zündkirsche"—ignition cherry) is made from 15 parts by weight of barium peroxide and 2 parts of powdered magnesium metal, intimately mixed and held together with collodion. The whole is wrapped with magnesium ribbon, a piece of the ribbon serving as the fuse. Magnesium burns with the evolution of much heat; the barium peroxide furnishes the large amounts of oxygen needed for such forced combustion (H. Blücher, Auskunftsbuch für die chemische Industrie [Data Book for the Chemical Industry], 18th ed., de Gruyter, Berlin, 1954, p. 1314).

fritted-glass funnel. The dark-colored filtrate is transferred to a 500-ml. three-neck flask, carefully prepurged with N_2. The solution is covered with 200 ml. of benzene, and 10 g. of potassium diaminomethanedisulfinate $(NH_2)_2C(SO_2K)_2$ [or the same amount of formamidinesulfinic acid $(NH_2)_2CSO_2$] is added with vigorous stirring. Next, 60 ml. of conc. ammonia is added (under a protective nitrogen atmosphere). This gives rise to a green color in the nascent suspension, as well as in the benzene. After two hours of stirring, the green benzene solution is decanted (in the absence of air) into a fairly large Schlenk tube (see Part I, p. 75) which has been carefully prepurged with N_2; it is then dried with solid KOH.

A green crystalline residue remains after vacuum removal of the benzene. This is transferred to a sublimation vessel (complete exclusion of air) and sublimed in high vacuum at 100–105°C.

Yield: with $(NH_2)_2C(SO_2K)_2$, 1 g.; with $(NH_2)_2CSO_2$, 0.7 g.; or 27 and 20% of theoretical, respectively (based on $MoCl_5$).

PROPERTIES:

Green crystals, extremely sensitive to air; decomp. 115°C. Soluble in organic media such as benzene, ether and petroleum ether. Insoluble in water. Very sensitive to oxidation.

REFERENCE:

DropBooks

E. O. Fischer and H. O. Stahl. Chem. Ber. 89, 1805 (1956).

Molybdenum (II) Chloride

Mo_3Cl_6

I. $$\underset{1213.9}{6\,MoCl_5} = \underset{500.6}{Mo_3Cl_6} + \underset{713.3}{3\,MoCl_4}$$

Heating of 20 g. of pure $MoCl_5$ to red heat in a small boat placed in an O_2-free nitrogen stream gives bright yellow, analytically pure Mo_3Cl_6 (93% yield).

II. $$\underset{288.0}{3\,Mo} + \underset{296.8}{3\,COCl_2} = \underset{500.6}{Mo_3Cl_6} + 3\,CO$$

A stream of $COCl_2$ (3 bubbles/sec.) is allowed to react with 8 g. of very pure Mo in a Vycor tube (30 minutes at about 610°C). Yield is 90%; 0.5% is lost in the form of side products; the remainder is unreacted Mo. Heating is carried out with a thermostatically controlled electric furnace precalibrated to 610°C.

The sintered reaction mass is finely ground and extracted several times with a mixture of 95 parts of ether and 5 parts of alcohol (reflux). The filtered, golden-yellow solution gives (in vacuum) a scalelike residue which crumbles to a light-yellow dust when ground. This compound corresponds to the formula $Mo_3Cl_8 \cdot C_2H_5OH$; the alcohol cannot be removed without decomposing the product.

PROPERTIES:

Amorphous, dull-yellow powder, stable in air. Infusible, nonvolatile; d_4^{25} 3.714. Insoluble in water, glacial acetic acid, toluene and naphtha. Soluble in alcohols, acetone and pyridine.

REFERENCES:

I. W. Biltz and C. Fendius. Z. anorg. allg. Chem. 172, 384 (1928); S. Senderoff and A. Brenner. J. Elektrochem. Soc. 101, 28 (1954).
II. K. Lindner, E. Haller and H. Helwig. Z. anorg. allg. Chem. 130, 210 (1923).

Molybdenum (III) Chloride

$MoCl_3$

$$\underset{273.2}{MoCl_5} + \underset{22.4\ l.}{H_2} = \underset{202.3}{MoCl_3} + 2\,HCl$$

The reaction tube shown in Fig. 320 is used both for the preparation of $MoCl_5$ (see p. 1405) and the subsequent reduction to $MoCl_3$.

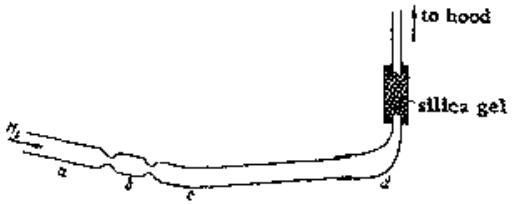

Fig. 320. Preparation of molybdenum (III) chloride. The lengths of the individual tube sections are: *a* 32 cm., *b* 8 cm., *c* 60–75 cm. The I.D. is 2–2.5 cm., 1–1.2 cm. at the constrictions.

Six grams of Mo powder is placed at *a*, and $MoCl_5$ is prepared from it (see next preparation); the product is then sublimed into *b* and *c* by means of a Cl_2 stream. After cooling, the Cl_2 is displaced with CO_2, and this, in turn, with dry, O_2-free hydrogen. The left end (near its lowest part) of zone *c* is now heated to about 250°C, so that a 5- to 10-cm. section of the tube is filled with red vapor. After some time, a white mist of HCl appears at the tube end adjacent to the moisture-retaining silica gel tube. Continued volatilization of the $MoCl_5$ (which keeps dropping into the lowest section of the tube) results in a copper-red coating.

The heat source is gradually shifted to the right, until all the $MoCl_5$ is transformed into $MoCl_3$. Overheating should be scrupulously avoided. The reaction requires 2–3 hours. At the end, the H_2 is replaced by dry CO_2, and the remaining $MoCl_5$ is distilled from section *b* so that none of it remains in the $MoCl_3$. The excess $MoCl_5$ is driven into adapter *d* (this tube is attached to the reactor by means of an asbestos seal). After cooling, the reactor tube is cut into several pieces and the crystals are pushed out with a glass rod. Yield: 4–6 g.

PROPERTIES:

Copper- to brown-red powder; d_4^{25} 3.578. Stable in air; sparingly soluble in pyridine; insoluble in water, alcohol and ether. Forms a blue solution with conc. H_2SO_4.

DropBooks

REFERENCES:

H. Biltz and W. Biltz. Übungsbeispiele aus der unorganischen Experimentalchemie [Excercises in Inorganic Experimental Chemistry], 3rd and 4th eds., 1920; W. Biltz and C. Fendius, Z. anorg. allg. Chem. 172, 389 (1928); L. P. Liechti and B. Kempe, Liebigs Ann. 169, 344 (1873); see also A. Rosenheim, G. Abel and R. Lewy, Z. anorg. allg. Chem. 197, 200 (1931).

Molybdenum (V) Chloride

$MoCl_5$

$$\underset{191.9}{2\,Mo} + \underset{110.0\,l.}{5\,Cl_2} = \underset{548.5}{2\,MoCl_5}$$

The apparatus shown in Fig. 321 is used for the chlorination of the Mo. During the experiment, an additional large-diameter piece of glass tubing is attached at *c* by means of a large-diameter

rubber hose. This glass tube is pointed upward. The left section of reaction tube a–b is charged with 6–10 g. of Mo (for preparation, see p. 1401). Then CO_2 and H_2 (both free of oxygen and very dry) are passed through the tube until the air is completely displaced from a wash bottle which is connected in series. The CO_2 flow is now shut off, and the Mo heated in the hydrogen stream for 1–2 hours (the temperature should be as high as possible). The water (which forms via reduction of the surface oxide layer) is driven off via the open end c by means of a burner and the tube is allowed to cool in the H_2 stream.

The oxide layer may also be reduced in an alternate procedure, whereby the Mo is heated in a dry HCl stream until no further wooly sublimate ($MoO_3 \cdot 2\,HCl$) is formed. The sublimate can be driven into the above mentioned glass tube by gentle warming (use a hood!). It is recommended that a drying tube or a wash bottle with conc. H_2SO_4 be attached at the end of the reaction tube to maintain anhydrous conditions. The outlet gases should pass through the drying arrangement before entering the hood.

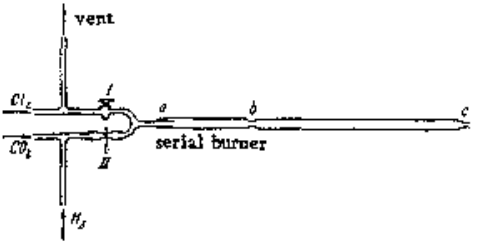

Fig. 321. Preparation of molybdenum (V) chloride. Overall length of reaction tube about 1 m.; part a–b 30 cm.; I.D. 2–2.5 cm. and 1–1.2 cm. at the constrictions.

Before chlorination, the tube is cooled, the attached wash bottle (conc. H_2SO_4) purged of air with Cl_2, and the H_2 (or HCl) displaced from the tube with Cl_2; during this operation, pinchcock II remains closed. The reaction between Mo and Cl_2 either starts spontaneously or at most needs only very gentle heating with a serial burner for initiation. The reaction is accompanied by the appearance of streams of deep dull-red vapor which condense beyond the constriction b. By gentle heating of the Mo with a serial burner, as well as occasional heating of constriction b by fanning with a Bunsen flame, the $MoCl_5$ is collected in b–c, where it precipitates in a shower of very fine crystalline leaflets. Intense heating must be avoided. At the end, only a few small gray flakes remain at the left of b.

The tube contents are allowed to cool in a CO_2 stream, *c* is closed off with a cork, and *b* is sealed off with a torch. The crystals are loosened by tapping, and transferred to a CO_2-filled, 35-cm-long storage tube of the same diameter as the combustion tube (the storage tube is slipped over constriction *c*). The storage tube is then sealed off.

PROPERTIES:

Blue-black, extremely hygroscopic crystals; dark green if oxychloride is present. M.p. 194°, b.p. 268°; d^{25}_4 2.927$_s$. Soluble in water and alcohol (solvolysis); soluble without decomposition in organic solvents such as ether, $CHCl_3$, CCl_4 and CS_2.

REFERENCES:

H. Biltz and W. Biltz. Übungsbeispiele aus der unorganischen Experimentalchemie [Exercises in Inorganic Experimental Chemistry], 3rd and 4th eds., 1920, p. 216; W. Biltz and A. Voigt. Z. anorg. allg. Chem. 133, 299 (1924); P. Liechti and B. Kempe. Liebigs Ann. 169, 345 (1873); E. R. Epperson et al. Inorg. Syntheses 7, 163 (1963).

DropBooks

Molybdenum (III) Bromide

$MoBr_3$

$$2\,Mo + 3\,Br_2 = 2\,MoBr_3$$
$$191.9 \quad 479.5 \quad 671.4$$

Obtained (75% yield) by heating Mo in a stream of Br_2 at 350°C. Separated from by-products by washing in cold, HBr-saturated water.

PROPERTIES:

Formula weight 335.70. Black, densely matted crystalline needles, which decompose to Mo_3Br_8 and Br_2 when calcined in the absence of air. Insoluble in water and acids, readily soluble in boiling anhydrous pyridine, forming $[MoBr_3py_3]$.

REFERENCE:

A. Rosenheim, G. Abel and R. Lewy. Z. anorg. allg. Chem. 197, 200 (1931).

Tribromotripyridinemolybdenum

[$MoBr_3py_3$]

$$\underset{335.7}{MoBr_3} + 3py = \underset{573.0}{[MoBr_3py_3]}$$

Five grams of $MoBr_3$ (see preceding preparation) is refluxed at 120°C with 20 g. of anhydrous pyridine (frequent swirling necessary). The hot pyridine solution is rapidly filtered (suction) to remove a small amount of residue and is then treated with conc. HCl until a weak acid reaction is obtained. The brown-yellow precipitate which forms is filtered off and washed with alcohol and ether. For purification the compound is extracted with chloroform in a Soxhlet apparatus. Crystal clusters consisting of small octahedra separate upon slow evaporation of the solution.

PROPERTIES:

Brownish-yellow needles; crystallize in octahedra from chloroform; soluble in pyridine; sparingly soluble in chloroform; insoluble in water, dilute acids, alcohol and ethyl acetate.

REFERENCE:

A. Rosenheim, G. Abel and R. Lewy. Z. anorg. allg. Chem. 197, 201 (1931).

Potassium Hexachloromolybdate (III)

K_3MoCl_6

$$\underset{(-2\,H_2O)\ 360.0}{2\,MoO_3} + 6\,HCl + 6\,KCl + 6\,e \rightarrow \underset{652.0}{2\,K_3MoCl_6}$$
$$\underset{447.3}{}$$

1. A solution of 20 g. of $H_2MoO_4 \cdot H_2O$ in 150 ml. of conc. HCl and 50 ml. of distilled water is electrolyzed for several hours at about 0.06–0.12 amp./in.^{2}; the electrolysis vessel is water cooled and CO_2 is bubbled through the solution. The solution is thus reduced to the red, trivalent state.

Smooth Pt, Hg or amalgamated Pb may be used for the cathode. The carbon anode, immersed in 15% HCl, is separated from the cathodic electrolyte by a clay cell diaphragm.

The reduced solution is evaporated as rapidly as possible over a free flame until its volume is about 90 ml.; it is then saturated

with hydrogen chloride and treated with a deaerated 10% solution of 15–20 g. of KCl in distilled water. It is then concentrated at 70°C and reduced pressure until crystals begin to separate, filtered and resaturated with hydrogen chloride while cooling in ice. The crystals are suction-filtered, washed with conc. HCl, with alcoholic HCl and finally with alcohol; they are then dried in vacuum.

II. Potassium molybdate is dissolved in HCl and reduced at a cathode immersed in a clay cell. Gaseous HCl is bubbled through the cathode liquor to precipitate the K_3MoCl_6.

PROPERTIES:

Formula weight 425.98. d^{18} 2.54. Brick-red crystals, readily soluble in water.

REFERENCES:

I. W. R. Bucknall, S. R. Carter and W. Wardlaw, J. Chem. Soc. (London) 1927, 513; A. Rosenheim and W. Braun, Z. anorg. Chem. 46, 320 (1905).
II. S. Senderoff and A. Brenner, J. Electrochem. Soc. 101, 28 (1954); see also K. H. Lohmann and R. C. Young in: J. C. Ballar, Inorg. Syntheses, Vol. IV, New York–London–Toronto, 1953, p. 97.

PrepBooks

Molybdenum (IV) Oxide

MoO_2

I.

$$\underset{144.0}{MoO_3} + \underset{22.4\ l.}{H_2} = \underset{128.0}{MoO_2} + \underset{18.0}{H_2O}$$

Molybdenum (VI) oxide is reduced for 5–7 hours in a stream of H_2 at 450°C; the oxide mixture is then calcined at dark-red heat in a porcelain boat while a stream of HCl is passed over it; this causes any remaining MoO_3 to volatilize as $MoO_3 \cdot 2\,HCl$. Finally the product is allowed to cool under H_2.

II. MELT REDUCTION OF MoO_3 WITH NH_3

The following method is useful for preparing pure MoO_2: Eight grams of dehydrated commercial ammonium molybdate, 7 g. of purified molybdic acid, 14 g. of calcined K_2CO_3, and 7 g. of H_3BO_3 are fused together in a large-capacity, covered Pt crucible and kept in the molten state for several hours. Cooling yields a

brittle cake, permeated with beautiful MoO_2 crystals; this is easily removed from the crucible. The pure crystals are readily separated by a simple extraction of the melt with boiling water.

III. A mixture of MoO_3 and Mo (2:1 mole ratio) is heated for 40 hours at 700°C in the absence of air.

PROPERTIES:

Brown-violet powder or crystals, insoluble in water; d^{25}_4 4.696. Crystal structure: C 4 (rutile) type.

REFERENCES:

I. C. Friedheim and M. K. Hoffmann. Ber. dtsch. chem. Ges. 35, 792 (1902).
II. W. Muthmann. Liebigs Ann. 238, 116 (1887).
III. A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Analyt. Chem. 24, 1998 (1952).

γ-Molybdenum Oxide

Mo_4O_{11}

$$11\,MoO_3 + Mo = 3\,Mo_4O_{11}$$
$$1583.5 \quad 96.0 \quad 1679.4$$

Very pure molybdenum powder and sublimed MoO_3 are intimately mixed and charged into a preignited alumina crucible, which is placed at the sealed end of a quartz tube. The mixture is degassed in high vacuum, purged frequently with O_2-free argon, and then heated for 3 days at 580°C under an argon pressure of 150 mm. The product is allowed to cool, the material is reground to a fine powder, and reheated for 3 days in the same manner.

PROPERTIES:

Formula weight 559.80. Violet crystalline powder. Relatively stable to acids and alkalies. Concentrated HNO_3 causes slow oxidation to MoO_3. Semiconductor material. d^{20}_4 4.18. Orthorhombic crystals (space group D^{18}_{2h}).

REFERENCES:

G. Hägg and A. Magnéli. Ark. Kem. Mineral., Geol. 19 A, 1 (1944); O. Glemser and G. Lutz. Z. anorg. allg. Chem. 263, 2 (1950); A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Analyt. Chem. 24, 1998 (1952).

Lower Molybdenum Hydroxides

MOLYBDENUM BLUE, $Mo_4O_{11}(OH)_2$

Obtained by reaction of nascent hydrogen with MoO_3.

Fifty ml. of distilled water and 10 ml. of conc. HCl, followed by 3 g. of analytically pure zinc granules, are added to 10 g. of MoO_3. The mixture is left standing overnight; the blue precipitate is then filtered off, washed until no chloride reaction is evident, and dried over P_2O_5.

Alternate methods: a) Reduction with $SnCl_2 \cdot 2\,H_2O$ in HCl solution.

b) Synthesis from MoO_3 and Mo powder (O. Glemser and G. Lutz, see below).

Other molybdenum blue compounds: See O. Glemser and G. Lutz (below).

PROPERTIES:

Formula weight 477.82. Blue crystalline powder. In air, oxidizes very slowly to MoO_3. Stable to NH_3 and alkalies. Good electrical conductivity.

DropBooks

REFERENCE:

O. Glemser and G. Lutz, Z. anorg. allg. Chem. 264, 17 (1951).

$Mo_5O_6(OH)_{10}$

This olive-colored hydroxide is obtained by the action of zinc granules on molybdenum trioxide in conc. HCl.

An Erlenmeyer flask is fitted with a water-filled valve to exclude air (Contat-Göckel attachment), whereupon 1 g. of MoO_3 is charged; 100 ml. of conc. HCl is then added, followed by about 50 g. of zinc granules. The solid phase first becomes blue [formation of $Mo_4O_{10}(OH)_2$ and $Mo_2O_4(OH)_2$], then red [$Mo_5O_7(OH)_6$], and after about one hour green [$Mo_5O_5(OH)_{10}$]. It is desirable to cool the flask with ice during the reduction. The $Mo_5O_5(OH)_{10}$ is extremely sensitive to air; the latter must therefore be excluded during washing with water. The compound is dried with O_2-free nitrogen and stored in sealed tubes.

PROPERTIES:

Oxidizes instantly in air, evolving heat. Evolves hydrogen on thermal decomposition in vacuum, forming Bordeaux red $Mo_5O_7(OH)_6$. This is also the main product obtained in the reaction of aerated water with $Mo_5O_5(OH)_{10}$.

REFERENCE:

O. Glemser, G. Lutz and G. Meyer. Z. anorg. allg. Chem. 285, 173 (1956).

Molybdenum (VI) Oxide

MoO_3

Prepared from ammonium molybdate and nitric acid.

Boiling conc. nitric acid is added to a boiling solution of pure, recrystallized ammonium molybdate, thus precipitating H_2MnO_4. After standing for several hours, the granular precipitate is filtered off on a Büchner funnel, washed and dried for 16-20 hours at above 150°C, whereupon it dehydrates to MoO_3. The MoO_3 may be purified by sublimation in a quartz tube at 780°C.

SYNONYMS:

Molybdenum trioxide; molybdic anhydride.

PROPERTIES:

Formula weight 143.95. White powder, turning yellow on heating and reverting to white on cooling. The sublimed product consists of sparkling, colorless crystalline flakes. M.p. 795°C, b.p. 1155°C; d_4^{26} 4.696. Solubility at 28°C: 0.490 g. MoO_3/liter H_2O. Crystal form: rhombic. Space group V_h^{16}.

REFERENCES:

W. C. Schumb and W. H. Hartford. J. Amer. Chem. Soc. 56, 2613 (1934); O. Königschmid and G. Wittmann. Z. anorg. allg. Chem. 229, 86 (1936).

Molybdic Acid

$H_2MoO_4 \cdot H_2O$

Prepared from ammonium molybdate and nitric acid.

An aqueous solution of ammonium molybdate (150 g./liter) is poured into 1 liter of 30% nitric acid [300 ml. of conc. HNO_3 (d 1.42) per liter] at room temperature (vigorous stirring). Then 200 g. of solid NH_4NO_3 is dissolved in the clear liquid, which is then seeded with a few granules of $H_2MoO_4 \cdot H_2O$. On standing

8-10 days $H_2MoO_4 \cdot H_2O$ separates in almost theoretical yield. The acid is washed for several days by repeated decantation with ice water.

PROPERTIES:

Formula weight 179.98. Transparent canary-yellow crystals, very sparingly soluble in water. Loses 1 mole of H_2O by standing for about 2 weeks in vacuum over H_2SO_4. d^{18} 3.124. Monoclinic-prismatic crystals.

REFERENCE:

A. Rosenheim. Z. anorg. Chem. 50, 320 (1906).

Ammonium Oxopentachloromolybdate (V)

$(NH_4)_2[MoOCl_5]$

$$\underset{287.9}{2\,MoO_3} + 6\,HCl + \underset{214.0}{4\,NH_4Cl} + 2\,e \rightarrow \underset{650.6}{2\,(NH_4)_2[MoOCl_5]}$$

A) PREPARATION OF MoO_3 SOLUTION

The MoO_3 (100 g.) is dissolved in HCl (d 1.16, 500 ml.) by heating. The solution is concentrated to 250 ml., filtered and made up to 500 ml. with HCl.

DropBooks

B) ELECTROLYTIC REDUCTION

The above-prepared solution (75 ml.) is diluted with an equal volume of H_2O and electrolyzed at a platinized Pt cathode (surface = 5 $cm.^2$) at 2.5 amp. until hydrogen evolves. The anode is made of smooth Pt sheet; it is immersed in 5 N HCl, which is separated from the cathode space by means of a clay cell.

The resulting red-brown solution is vacuum-concentrated to 50 ml. and treated with a solution of 9 g. of NH_4Cl in 30 ml of water; the mixture is heated for about one minute.

Hydrogen chloride is introduced while cooling the flask and emerald-green crystals are precipitated. These are recrystallized by dissolving in a minimum quantity of water at 80°C and saturating the solution with HCl while cooling. The crystals are washed with conc. HCl and dried in vacuum over KOH.

PROPERTIES:

Formula weight 325.32. Emerald-green octahedral crystals, which dissolve in water with hydrolysis and development of brown color.

REFERENCES:

R. G. James and W. Wardlaw. J. Chem. Soc. (London) 1927, 2146; F. Foerster and R. Fricke. Z. angew. Chem. 36, 458 (1923).

Potassium Hydrogen Diperoxomonomolybdate

$KHMoO_6 \cdot 2H_2O$

Potassium molybdate solutions rich in H_2O_2 are treated with one equivalent of mineral acid per mole of molybdate, whereupon $KHMoO_6 \cdot 2\ H_2O$ crystallizes.

PROPERTIES:

Formula weight 268.09. Long, pale yellow, crystalline needles.

REFERENCES:

K. F. Jahr. Ber. Ges. Freunde TH. Berlin 1939, 91; K. F. Jahr. Naturforsch. u. Medizin in Deutschland [Scientific Research and Medicine in Germany] 1939-1946 (FIAT Review) 25, III, 189.

Tetraamminezinc Tetraperoxomolybdate (VI)

$[Zn(NH_3)_4]MoO_8$

Prepared from ammonium molybdate, NH_4OH and $ZnSO_4$ by addition of H_2O_2.

A mixture of 100 ml. of water, 100 ml. of conc. ammonia (d 0.91), and 20 ml. of an ammonium molybdate solution containing 1 g.-atom of Mo per liter is cooled to −12°C in an ice-salt mixture. Lower temperatures cannot be used, since water is frozen out (ice) at −14°C. Then 30 ml. of Perhydrol (30% H_2O_2) is added, followed by 20 ml. of 1 M $ZnSO_4$ solution (brief but thorough stirring). The solution is allowed to stand undisturbed for 1.5 hours at −12°C. After one half hour it is examined for signs of incipient crystallization. If none is observed, crystal formation is induced by careful rubbing of the flask walls with a glass rod. The crystals are filtered off, washed twice with ice-cold 96% alcohol and then twice with ice-cold ether. Yield: about 3 g.

PROPERTIES:

Formula weight 357.46. Deep red-brown, lustrous crystals; soluble in water (decomposition). Ammoniacal solutions are more

stable. Insoluble in organic solvents. Appreciably more stable than the corresponding potassium salt and barely explosive. However, it is not advisable to seal it into ampoules. May be stored in a desiccator over KOH and under NH_3 for about 1 week.

REFERENCE:

K. Gleu. Z. anorg. allg. Chem. 204, 73 (1932).

Molybdenum (IV) Sulfide

MoS_2

I. $$\underset{128.0}{MoO_3} + 3\,S = \underset{160.1}{MoS_2} + SO_2$$

A mixture of 150 g. of K_2CO_3, 310 g. of S, and 200 g. of MoO_3 is heated at red heat for one half hour. After cooling and extracting with water, the residue is 80 g. of MoS_2. It is also possible to start with 200 g. of ammonium molybdate, 150 g. of K_2CO_3, and 280 g. of S; this affords a more crystalline product, although in lower yield. According to Bell and Herfert, one may also start with MoO_3, K_2CO_3 and S.

DropBooks

II. $$\underset{96.0}{Mo} + 2\,S = \underset{160.1}{MoS_2}$$

Stoichiometric quantities of Mo and S are heated in an iron tube. The MoS_2 thus obtained has the crystal lattice of natural molybdenite.

SYNONYM:

Molybdenum disulfide.

PROPERTIES:

Opaque, gray-blue leaflets with a greasy feel, or graphite-like powder. Sublimes at 450°C; d^{15} 5.06. Soluble (decomposition) in aqua regia. Decomposed by H_2SO_4 to MoO_3. Electrical conductor whose conductivity increases with illumination. Diamagnetic. Crystal structure: C 7 type.

REFERENCES:

I. M. Guichard, Comptes Rendus Hebd. Séances Acad. Sci. 129, 1239 (1899); Ann. Chim. Phys. 7, 23, 552 (1901); R. E. Bell and R. E. Herfert. J. Amer. Chem. Soc. 79, 3351 (1957).
II. A. E. van Arkel. Recueil Trav. Chim. Pays Bas 45, 442 (1926).

Ammonium Tetrathiomolybdate

$(NH_4)_2MoS_4$

Prepared by treating an ammoniacal ammonium molybdate solution with H_2S.

A solution of 5 g. of $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ in 15 ml. of water is prepared and treated with 50 ml. of ammonia (d 0.94). Then H_2S is introduced. The solution first turns yellow, later deep red, and after half an hour a copious quantity of crystals, some of them well-formed, precipitates suddenly. The crystals are washed with cold water, then with alcohol, and dried in vacuum.

PROPERTIES:

Formula weight 260.27. Blood-red crystals with metallic surface luster, readily soluble in water, very sparingly soluble in alcohol.

REFERENCE:

G. Krüss. Liebigs Ann. 225, 29 (1884).

Potassium Octacyanomolybdate (IV)

$K_4[Mo(CN)_8] \cdot 2\,H_2O$

I. A solution of Mo (III) obtained by electrolytic reduction is oxidized to the quadrivalent state with a stoichiometric quantity of MoO_3 and is then treated with NH_4SCN and pyridine. The precipitate is converted to $K_4[Mo(CN)_8] \cdot 2\,H_2O$ by reaction with KCN.

A solution of 15 g. of pure MoO_3 in 150 ml. of 8 N HCl is reduced to the trivalent state at a lead cathode (5–10 amp.) while cooling the cathode cell (porous clay) with water and bubbling CO_2 through the solution. A graphite rod immersed in 15% HCl serves as the anode.

The reduced solution is treated with a solution of 7.5 g. of MoO_3 in 75 ml. of 8 N HCl; the solution thereby changes from red to green. The Mo (IV) salt solution thus obtained is poured into a concentrated solution of 95 g. of NH_4SCN; 60 g. of pyridine is added, and the solution is made weakly alkaline with ammonia. These reactions are best carried out under CO_2 in the absence of air.

A black oil separates during the neutralization; this solidifies to a solid black tar on cooling with ice. The supernatant liquid is decanted; the tar is washed with water and added slowly to a hot,

saturated 10 M KCN solution. The reaction mixture is concentrated until crystals begin to deposit; it is then cooled in ice and filtered with suction.

The mother liquor is further concentrated and the cyano complex is precipitated with alcohol (rapid stirring). The crude product is dissolved in some water, the solution heated for some time with activated charcoal, filtered, concentrated by evaporation, and finally treated with alcohol. The precipitate of $K_4[Mo(CN)_8] \cdot 2\,H_2O$ is fairly pure except for traces of thiocyanate, which can be removed by an additional recrystallization. Yield: about 55 g.

Alternate methods:

II. The product of the reaction of MoO_3 with HSCN and pyridine is treated with KCN. The yield is low. (See original reference for details.)

III. Via the following intermediates:

$$MoO_3 \xrightarrow{HCl,\ H_2O} H_2MoO_4 \xrightarrow{KSCN} Mo(OH)_2(SCN)_3 \xrightarrow{\text{pyridine}} Mo(OH)_2(SCN)_3 \cdot 2\,py \xrightarrow{KCN} K_4[Mo(CN)_8] \cdot 2\,H_2O$$

PROPERTIES:

Formula weight 496.50 (dihydrate). Golden or bright-yellow tablet-shaped crystals (rhombic bipyramidal); gives up its water of crystallization at 105–110°C. Very readily soluble in water, insoluble in ether. Solubility in absolute alcohol at 20°C: 0.017 g. per liter. d_4^{25} (anhydrous salt) 2.337.

DropBooks

REFERENCES:

I. H. H. Willard and R. C. Thielke. J. Amer. Chem. Soc. 57, 2610 (1935).

II. A. Rosenheim. Z. anorg. Chem. 54, 97 (1907); see also W. Biltz, E. Eschweiler and A. Bodenstein. Z. anorg. allg. Chem. 170, 168 (1928).

III. N. H. Furman and C. O. Miller in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 160.

Tungsten

W

$$\underset{231.9}{WO_3} + \underset{67.3\,l.}{3\,H_2} = \underset{183.9}{W} + \underset{54.1}{3\,H_2O}$$

Pure ignited WO_3 is placed in a porcelain or, better, a nickel boat, which is then inserted into a tube of unglazed porcelain or

other refractory material. The tube is heated by means of an electric furnace while passing through a stream of pure, dry H_2. The initial temperature is 800°C (maintained for some time), later 1000–1200°C. The reduction proceeds fairly rapidly and is complete when no further H_2O vapor evolves. The tube is allowed to cool in the H_2 stream. Gray metal powder is the product.

Other authors report that the reduction with very pure H_2 may even be completed at 800°C (8 hours of heating).

The particle size of the metal powder does not depend on that of the starting WO_3, but (principally) on the reaction temperature, as well as the heating time and the H_2 flow rate. An especially fine tungsten powder is obtained when the above directions are followed; a very coarse powder results from reduction with moist H_2 above 1500°C. The product is pure if the starting WO_3 is also pure.

Alternate method:

$$\underset{231.9}{WO_3} + \underset{196.1}{3\,Zn} = \underset{183.9}{W} + \underset{244.1}{3\,ZnO}$$

Pure, freshly ignited WO_3 is cooled and mixed with 1.5 times the theoretical quantity of dry Zn dust. This mixture is compressed in a crucible and overlaid with another 3- to 5-mm. layer of Zn dust, which is similarly compressed. The crucible is then closed off with a well-fitting cover and heated briefly to red heat. A vigorous reaction ensues after about 5 minutes, as shown by a cloud of evolving ZnO. The crucible is then allowed to cool completely while still covered. The light-gray top layer, composed principally of ZnO, is removed. The black crucible contents are crushed and thoroughly boiled with dil. HCl to remove ZnO and any Zn still present. The black residue is allowed to settle for a moment and the acid is decanted. The metal powder is washed by decantation with water once or twice, filtered rapidly with suction, and rewashed with water. In this operation the powder must always be covered with liquid. Finally the metal is washed with alcohol, suction-filtered, and dried in air. Careful preparation should yield a black powder containing at least 99.8% W.

SYNONYM:

Wolfram.

PROPERTIES:

Tungsten powder is gray to black, depending on particle size; the solid exhibits a light gray, lustrous surface. M.p. ~ 3650°C, b.p. > 5000°C (calculated from the vapor pressure curve); d 19.3. Hardness 4.5–8, depending on the history. Crystal structure: A 2 type.

REFERENCES:

H. Funk. Darstellung der Metalle im Laboratorium [Preparation of Metals in the Laboratory], Stuttgart, 1938, p. 72 f.; O. Ruff. Angew. Chem. 25, 1892 (1912); O. Glemser and H. Sauer. Z. anorg. allg. Chem. 252, 145 (1943); M. Delépine. Comptes Rendus Hebd. Séances Acad. Sci. 131, 184 (1900); L. Weiss and A. Martin. Z. anorg. allg. Chem. 65, 308 (1910).

Tungsten (V) Chloride

WCl_5

$$WCl_6 + {}^1/_2 H_2 = WCl_5 + HCl$$
$$396.7 \quad 11.2\,l. \quad 361.2$$

Reduction of WCl_6 vapor with H_2 for too short a period of heating and at too low a temperature results in hexachloride-containing WCl_5. Too high a temperature affects the yield adversely, since considerable amounts of lower chlorides form.

A tube of high-melting glass (Fig. 322) is used. The WCl_6 produced in section *a* is distilled into the 50-cm.-long section *b* in a stream of H_2. Section *b* is heated to the reduction temperature, which lies somewhat above the boiling point of WCl_6 (350–400°C, electric furnace). The WCl_5 is distilled into storage tube *c* in a stream of N_2, thereby separating it from the lower chlorides; tube *c* is then sealed off at both ends.

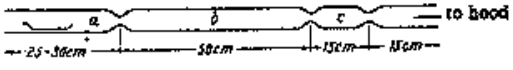

Fig. 322. Preparation of tungsten (V) chloride.

PROPERTIES:

Black, crystalline solid with somewhat greenish luster. Extremely hygroscopic. M. p. 248°C; d_4^{25} 3.875. Water causes immediate decomposition; somewhat soluble in dry CS_2.

REFERENCES:

H. E. Roscoe. Liebigs Ann. 162, 356 (1872); W. Biltz and A. Voigt. Z. anorg. allg. Chem. 133, 301 (1924); W. Biltz and C. Fendius. Ibid. 172, 385 (1928); W. Klemm and H. Steinberg. Ibid. 227, 193 (1936).

DropBooks

Tungsten (VI) Chloride

WCl_6

I.

$$\underset{183.9}{W} + 3\,\underset{66.01.}{Cl_2} = \underset{396.7}{WCl_6}$$

Prepared in a Vycor tube with several constrictions (Fig. 323). A quartz tube is even better and the special apparatus described by Hönigschmid and Menn is the best.

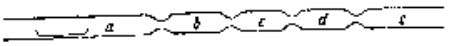

Fig. 323. Preparation of tungsten (VI) chloride.

A procelain or quartz boat containing W powder is placed in section *a* and is heated for 1-2 hours in a stream of H_2 (700-1000°C). After cooling, the H_2 flow is discontinued, the H_2 displaced by N_2; after about 30 minutes, air-free Cl_2 (see p. 272 for preparation) is introduced.

The tube area containing the boat is gradually heated to 600°C. The first product is a small amount of red oxychloride; later products consist only of blue-black hexachloride, which deposits in section *a* (beyond the heated boat) in the form of sparkling crystals. The tube constrictions are kept at 350-400°C during the chlorination, which requires 2-3 hours. Next the red oxychloride forerun is driven into *e*; then the WCl_6 collected in *a* is sublimed into *b* at 350-400°C, while an additional forerun deposits in *c*. For further purification, the WCl_6 can be sublimed into *c* (the oxychloride is moved into *d* prior to this sublimation). Finally, the WCl_6 is fused in a stream of Cl_2; on resolidification, the mass bursts into small crystals with a loud crackling noise. After cooling, the Cl_2 is displaced with dry, O_2-free nitrogen and the tube section containing the purified WCl_6 is sealed off at both ends.

II.

$$\underset{231.9}{WO_3} + 3\,\underset{461.5}{CCl_4} = \underset{396.7}{WCl_6} + 3\,\underset{296.8}{COCl_2}$$

The chief requirements in this method are the presence of an excess of CCl_4, completely anhydrous conditions, and thorough completion of the reaction; if these conditions are not observed, red by-product $WOCl_4$ forms readily. Moreover, the $WOCl_4$ has the undesirable property of catalyzing the hydrolysis of WCl_6 in moist air.

A dry glass bomb tube about 50 cm. long is charged with 0.5 g. of WO_3 and 11 g. of CCl_4 (the WO_3 must be completely dehydrated by previous ignition, after which it should be pure yellow; the CCl_4

is predried by long standing over granular $CaCl_2$ or P_2O_5 and is saturated with Cl_2). The tube is then sealed. The water vapor from the torch flame should not be allowed to enter the tube. The tube is placed in a protective iron jacket and slowly heated (1.5–2 hours) to about 450°C; it is kept at this temperature for 7–8 hours. After slow cooling, the tube is very carefully transferred to a well-drawing hood without removing it from its protective iron tube. The latter is inclined and clamped to a support. The sealed tip of the glass tube is then heated at low hood vacuum until the phosgene, present in the tube under high pressure, blows the tip away. The phosgene is driven out by vacuum as far possible, the CCl_4 poured off, the residual solid washed once with fresh CCl_4, and the reactor tube connected to an aspirator via a $CaCl_2$ drying tower. All the CCl_4 is volatilized and the tube is resealed since the beautiful, almost black crystals of WCl_6 hydrolyze in air to yellow-red $WOCl_4$ and yellow WO_2Cl_2. Proper procedure yields an almost black solid with no red or yellow spots.

PROPERTIES:

Blue-black, moisture-sensitive crystals. M.p. 275°C, b.p. 347°C; d_4^{25} 3.520. Indefinitely stable if stored in a dark desiccator over H_2SO_4. Very slightly soluble but decomposed in water; the purer the WCl_6, the lower the decomposition rate. Very readily soluble in alcohol (with yellow color), $CHCl_3$, CCl_4 (with red and dark-brown color, respectively), CS_2, ether, benzene, ligroin and acetone. These solutions decompose on long standing in air, and very rapidly on heating or addition of water. Good crystals are obtained by heating WCl_6 in CCl_4 to 100°C in a sealed tube, followed by slow cooling (rectangular tablets and four-sided prisms). Crystallizes in space group C_{3i}^2.

REFERENCES:

I. O. Hönigschmid and W. Menn. Z. anorg. allg. Chem. 229, 58 (1936); see also M. H. Lietzke and M. L. Holt in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 163.

II. W. Jander. Lehrbuch für das anorganisch-chemische Praktikum [Lab. Text for Inorg. Chemistry], 5th ed., Leipzig, 1944, p. 403.

Tungsten (IV) Oxide

WO_2

$$\underset{231.9}{WO_3} + \underset{22.4\,l.}{H_2} = \underset{215.9}{WO_2} + \underset{18.0}{H_2O}$$

Stable at 900°C in a gaseous atmosphere composed of 40–55% H_2 and 45–60% H_2O.

I. Pure H_2 is subjected to an additional purification over silica gel and is then slowly passed through a water-filled flask to saturate it with water vapor. The flask is held in an 85°C thermostat. To avoid condensation of the water vapor thus taken up, the tube which connects the flask to the reactor is wrapped with electric heating tape and heated to about 100°C. The H_2/H_2O mixture then flows over a boat with WO_3 set in a porcelain or a quartz reactor tube surrounded by a tubular electric furnace and heated to 800-900°C. The reduction is complete in 2 hours. The product is allowed to cool in an O_2-free nitrogen stream. The nitrogen is admitted through a 3-way stopcock located between the water flask and the reactor.

II. A mixture of WO_3 and W (corresponding to the formula $WO_{2.90}$) is heated for 40 hours at 950°C in a small evacuated and sealed quartz tube.

PROPERTIES:

Brown crystalline powder. M.p. 1500-1600°C under N_2, b.p. 1730°C; appreciably volatile above 1050°C; d^{25}_4 11.05. Hardness 5-5.5. Crystal structure: C 4 (rutile) type.

REFERENCES:

I. O. Glemser and H. Sauer. Z. anorg. allg. Chem. 252, 151 (1943); J. A. M. van Liempt. Ibid. 126, 184 (1923); L. Wöhler and R. Günther. Z. Elektrochem. 29, 281 (1923).
II. A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Analyt. Chem. 24, 1998 (1952).

γ-Tungsten Oxide

$W_{18}O_{49}$

$$49\,WO_3 + 5\,W = 3\,W_{18}O_{49}$$

1/10 1384.1 92.0 1468.1

Very pure W powder and very pure WO_3 are intimately mixed in the prescribed ratio of $WO_{2.72}$ and heated for 6 hours at 800°C in a small evacuated and sealed quartz tube. The product is ground and treated again for 24 hours at 800°C in the same manner.

PROPERTIES:

Formula weight 4853.47. Red-violet crystalline powder; semiconductor. d^{20}_4 7.72. Deformed $D0_9$ type.

REFERENCES:

O. Glemser and H. Sauer. Z. anorg. allg. Chem. 252, 144 (1943); A. Magnéli, Ark. Kem. 1, 223 (1949); A. Magnéli, G. Andersson, B. Blomberg and L. Kihlborg. Anal. Chem. 24, 1998 (1952).

Tungsten Blue

$H_{0.3}WO_3$

Produced by reaction of nascent hydrogen with WO_3.

Fine WO_3 powder is slurried with distilled water in an Erlenmeyer flask, conc. HCl and analytically pure Zn granules are added, and the flask is closed with a valve which excludes air (Contat-Göckel attachment). When the Zn is consumed, the supernatant liquid is rapidly decanted and fresh conc. HCl and Zn granules are added. This is repeated until the reaction product is brown. Washing, drying and transfer of the product to a storage vessel must be carried out in the absence of oxygen.

PROPERTIES:

Formula weight 232.42. Brown to violet powder; d_4^{20} 7.35. Very readily oxidized. Evolves H_2 along with H_2O on thermal decomposition. Oxidized by water with H_2 evolution. Slow oxidation affords blue $H_{0.33}WO_3$ and $H_{0.1}WO_3$. $D0_9$ type with tetragonal distortion.

DronBooks

REFERENCE:

O. Glemser and C. Naumann. Z. anorg. allg. Chem. 265, 288 (1951).

Tungsten (VI) Oxide

WO_3

I. $$\underset{(\cdot 2\,H_2O)\ 330.0}{Na_2WO_4} + 2\,HCl = \underset{72.9}{WO_3} + H_2O + 2\,NaCl \qquad \underset{231.9}{}$$

The yellow WO_3 is obtained by slow dropwise addition of a warm, saturated solution of Na_2WO_4 to 2–3 times its volume of boiling conc. HCl, followed by additional heating (for 1 hour) on a steam bath. The precipitate is allowed to settle, washed with

5% NH_4NO_3 solution until no further Cl^- reaction is obtained, and dried, first at 120°C and finally at 600°C.

PROPERTIES:

Lemon-yellow powder. M.p. about 1470°C, b.p. about 1700°C; d^{25} 7.27. Crystals triclinic, pseudomonoclinic. Space group C_1.

REFERENCE:

W. Reinders and A. W. Vervloet. Receuil Trav. Chim. Pay-Bas 42, 627 (1923).

Yellow Tungstic Acid

H_2WO_4

I. $$\underset{288.0}{CaWO_4} + 2HX = \underset{249.9}{H_2WO_4} + CaX_2$$

A boiling mixture of 50 ml. of H_2O, 40 ml. of conc. HCl, and 40 ml. of HNO_3 is treated with 20 g. of pure $CaWO_4$. The resulting yellow precipitate is washed 8 times by decantation with slightly acidified water, and dissolved in 50 ml. of conc. ammonia. The clear filtrate is heated to boiling and treated with acid (60 ml. of H_2O, 50 ml. of HNO_3 and 10 ml. of HCl) to precipitate yellow tungstic acid, which is washed several times by decantation with pure H_2O, filtered through a leaf filter and slurried in pure H_2O. The suspension settles on standing for 14 days, during which an electric current is occasionally passed through it (Pt electrodes); the clear supernatant liquid is siphoned off; the residue is concentrated on a steam bath and then thoroughly dried in a desiccator over solid NaOH. The tungstic acid product is free of HCl and has the composition $WO_3 \cdot 1.13\ H_2O$.

II. A boiling solution of 200 g. of ammonium tungstate [composition $2\ (NH_4)_2O,\ 0.5\ WO_3,\ 3\ H_2O$] in 4.48 liters of H_2O is poured into 2 liters of boiling 35.4% HCl. The deep-yellow precipitate is filtered off and purified by a nine-day dialysis (until the wash water is free of Cl^- and the pH has reached a constant value of 4.4). Air drying of the residue gives a 55% yield of tungstic acid of composition $WO_3 \cdot 1.18\ H_2O$; it still contains traces of NH_3 and Cl^-.

PROPERTIES:

Yellow powder, which appears amorphous under the microscope; it is claimed that its x-ray pattern is crystalline.

REFERENCES:

I. G. F. Hüttig and B. Kurbe, Z. anorg. allg. Chem. 122, 45 (1922).
II. A. M. Morley, J. Chem. Soc (London) 1930, 1990.

Tungsten Oxytetrachloride

$WOCl_4$

$$WO_3 + 2SOCl_2 = WOCl_4 + 2SO_2$$

I. A mixture of WO_3 with 4 times its weight of $SOCl_2$ is heated in a sealed tube for 6–12 hours at 200°C. The reaction proceeds to completion only if the SO_2 is vented by opening the sealed tube for a brief time. The red $WOCl_4$ crystallizes from the excess $SOCl_2$ in long, well-formed needles, and is purified by removing the $SOCl_2$ in vacuum.

II. A sealed tube is used to heat the WO_3 with a solution of Cl_2 in CCl_4 (3 hours at 200°C). The tube is cooled and opened (caution: phosgene is present!); the $WOCl_4$ is washed in the tube with dry CCl_4; and the tube and its contents are heated to 160°C and immediately placed in a desiccator.

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PROPERTIES:

Long, lustrous, red needles, yellow in transmitted light. M.p. 209°C, b.p. 232°C. Decomposed at once by water, more slowly by atmospheric moisture, forming tungstic acid.

REFERENCES:

I. H. Hecht, G. Jander and H. Schlapmann, Z. anorg. allg. Chem. 254, 261 (1947).
II. A. Michael and A. Murphy, Amer. Chem. J. 44, 382 (1910).

Tungsten (IV) Sulfide

WS_2

I.

$$\underset{183.9}{W} + \underset{64.1}{2S} = \underset{248.0}{WS_2}$$

A stoichiometric mixture of W and S is heated at 800°C under very pure N_2 in a sealed quartz tube for 24 hours.

II.

$$\underset{468.8}{2\,WO_3} + \underset{224.4}{7\,S} = \underset{496.1}{2\,WS_2} + \underset{192.2}{3\,SO_2}$$

An intimate mixture of 33 g. of WO_3, 40 g. of sulfur and 15 g. of K_2CO_3 is placed in a tubular crucible of unglazed porcelain (190 mm. long, 35 mm. I.D.) which is closed off with a perforated asbestos lid. The crucible is heated in a vertical tubular furnace at 600–700°C until the reaction is complete and the excess S has burned off. It is then heated for an additional 15 hours at 1400°C while H_2S is passed through. Large crystals of pure sublimed WS_2 are thus obtained.

Finely crystalline WS_2 is obtained from 92 g. of W powder and 35 g. of sulfur by following the above directions but heating only for 7 hours at 1450°C in a stream of H_2S.

PROPERTIES:

Blue-gray crystals with a metallic luster, insoluble in water; d_0^{19} 7.5. Crystal structure: C 7 type. Exhibits catalytic and radio-detector properties.

REFERENCES:

I. O. Glemser, H. Sauer and P. König, Z. anorg. Chem. 257, 241 (1948).
II. E. Tiede and H. Lemke, Ber. dtsch. chem. Ges. 71, 584 (1938).

Tungsten Hexaphenoxide

$W(OC_6H_5)_6$

$$\underset{396.7}{WCl_6} + \underset{564.7}{6\,HOC_6H_5} = \underset{955.3}{W(OC_6H_5)_6} + 6\,HCl$$

One wt. part of WCl_6 and about 10 parts of phenol are heated in a long, large test tube. Vigorous evolution of HCl begins as soon as the phenol melts. The tube is now heated over a small flame until the phenol boils. After some time the melt (which initially is brown-black even in thin layers) becomes deep red. Boiling is continued for a short time; the tube is then cooled while rotating it to distribute the melt on the walls of the vessel. The cooled melt is treated with some alcohol while crushing with a glass rod. The excess phenol dissolves in the alcohol and the product separates as a brick-red powder. It is filtered off with suction, washed with alcohol, and recrystallized from the latter.

SYNONYM:

Tungsten hexaphenolate.

PROPERTIES:

Dark-red needles or leaflets. M.p. 98°C. Readily soluble in CCl_4, CS_2, C_6H_6, etc. Relatively poorly soluble in cold alcohol.

REFERENCE:

H. Funk and W. Baumann. Z. anorg. allg. Chem. 231, 265 (1937).

Potassium Enneachlorditungstate (III)

$K_3W_2Cl_9$

Prepared by electrolytic reduction of a KCl-containing solution of WO_3 in conc. hydrochloric acid.

A solution of 10 g. of $WO_3 \cdot H_2O$ in a conc. solution of 7.5 g. of K_2CO_3 is prepared. This solution (volume of about 15 ml.) is added in 2 or 3 portions to 260 ml. of conc. HCl (40°C); the hydrate, which precipitates after each addition, is allowed to redissolve before the next portion is introduced. After complete solution is finally obtained, the liquid is quickly cooled to 0°C. The crystalline precipitate thus obtained is composed for the most part of KCl. The solution, filtered through a fritted glass funnel, contains 3-4% WO_3 as $H[WO_2Cl_3]$, and is used in electrolysis.

The cathode vessel is a porous clay cell of about 6.5 cm. I.D. and 21 cm. high; this is set in a heavy-wall 12.5-cm.-I.D. and 20-cm.-high glass cylinder and centered with the aid of a rubber stopper. The rubber stopper contains five holes: two for the symmetrically placed carbon anodes, two for glass tubes used for passing CO_2 through the anodic electrolyte (so as to decrease the Cl_2 concentration in the latter), and a fifth hole through which the electrolyte is introduced. A drain is provided at the bottom of the anode vessel to permit rapid emptying at the end of the run. The clay cell is closed off hermetically with a rubber stopper, which carries a gas-tight stirrer (Hg seal), the cathode lead, and an opening for removal of samples during the electrolysis. The anodic liquor is conc. hydrochloric acid, while the clay cell is charged with 450 ml. of the W (VI) solution described above. The latter is reduced at 40°C and a current density of 0.4 amp./in.^{2} until it turns yellow-green and the consumption of permanganate becomes constant.

The cathode is a 140-cm.^{2} Pb sheet, which may be amalgamated if necessary. Runs with amalgamated electrodes require a longer

time (up to 2 hours) than do those with pure Pb cathodes (80–90 min.), but the product solution is free of Pb.

To obtain reproducible results with Pb cathodes, the latter must be formed by alternating anodic and cathodic polarization in 2 N H_2SO_4; this is unnecessary with the amalgamated electrodes (because of the purely chemical reducing action of the cathode metal, it is best to admit the cathodic liquid only after the voltage has been applied). The Pb, which initially goes into solution and later reprecipitates, causes no problem either during electrolysis or in the later workup of the solution.

After the completion of the reduction, the cathode is carefully removed from the solution, the anode vessel rapidly emptied, and the cathodic liquid containing the precipitated crystals poured into an Erlenmeyer flask, where it is then saturated with HCl while chilling in ice-salt mixture. After 1–2 days, the crystalline precipitate is collected on a fritted-glass funnel, washed with some conc. hydrochloric acid, then with alcohol and ether, and dried in a stream of air. The yield is about 60% based on the $WO_3 \cdot H_2O$ used.

For purification, $K_3W_2Cl_9$ is reprecipitated with a readily soluble potassium salt. For example, 25 g. of $K_3W_2Cl_9$ is dissolved in 175 ml. of boiled cold water; the solution is filtered into an Erlenmeyer flask which contains 150–175 g. of solid KSCN. The flask is then shaken. A copious quantity of deep green to yellow-green crystals separates even during the filtration; the solution meanwhile turns red. After one hour of standing in the cold, the crystals are suction-filtered, washed a few times with very concentrated KSCN solution, then with hot 80% alcohol, and dried in air. The product is fairly stable and can be stored for months in dry air over H_2SO_4.

SYNONYM:

Potassium nonachloroditungstate (III).

PROPERTIES:

Formula weight 804.24. Small, dark-green tablets, yellow in transmitted light. Soluble in water, giving a dark-green color; very slightly soluble in alcohol. The aqueous solution oxidizes in air; the crystalline compound also oxidizes but more slowly.

REFERENCES:

O. Collenberg and A. Guthe. Z. anorg. allg. Chem. 134, 317 (1924); O. Collenberg and K. Sandved. Ibid. 130, 9 (1923); O. Olson-Collenberg. Ibid. 88, 50 (1914); W. Biltz. Ibid. 170, 164 (1928); H. B. Jonassen, A. R. Tarsey, S. Cantor and G. F. Helfrich in: Th. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 139.

Hexachlorotripyridineditungstate (III)

$W_2Cl_6py_3$

$$\underset{804.3}{K_3W_2Cl_9} + \underset{237.3}{3py} = \underset{223.7}{3KCl} + \underset{817.9}{W_2Cl_6py_3}$$

Ten grams of freshly recrystallized $K_3W_2Cl_9$ is refluxed in 150 ml. of dry pyridine for 6 hours (N_2 atmosphere). The red solution is filtered to remove the brown precipitate and treated with a large excess (10 volumes) of ether. This precipitates the dark-brown complex salt; it may be recrystallized from pyridine.

PROPERTIES:

Insoluble in water, somewhat soluble in ether and benzene. Diamagnetic. A corresponding aniline complex exists.

REFERENCE:

H. B. Jonassen, S. Cantor and A. R. Tarsey. J. Amer. Chem. Soc. 78, 271 (1956).

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Potassium Octacyanotungstate (IV)

$K_4[W(CN)_8] \cdot 2H_2O$

Prepared from $K_3W_2Cl_9$ and KCN.

A solution of 20 g. of $K_3W_2Cl_9$ in 150 ml. of cold, boiled water is prepared and treated on a water bath with 65 g. of KCN powder; this causes oxidation to W (IV), and the green color of the solution changes to red. The KCN should be added very carefully (shaking) over a period of 5 to 10 minutes.

The solution is now heated about two hours on the water bath, filtered (decolorizing charcoal being added if required) and evaporated until crystals begin to deposit. The first crystal fraction, consisting predominantly of KCl, is filtered off and discarded. The filtrate is diluted to 130 ml. and treated, while still warm, with 20–25 ml. of 95% alcohol. The $K_4[W(CN)_8] \cdot 2H_2O$ separates in lustrous, bright-yellow plates on sharp cooling in a freezing mixture. After one hour, 15 additional ml. of alcohol is added. The mixture is suction-filtered after standing for 12 hours in the cold. The product is washed with hot 80% alcohol. Yield: 60–70%, based on tungsten.

For purification, the compound is first precipitated twice from 50% aqueous solution by adding an equal volume of alcohol. It is then dissolved in 16% KCN solution and, after concentrating, allowed to stand at 0°C until crystallization is complete. The product is again reprecipitated with water and alcohol to remove traces of KCN.

PROPERTIES:

Formula weight 584.5. d_4^{25} 1.989. Bright-yellow crystalline powder; slow evaporation of a KCN solution affords large, yellow-red crystals. Very readily soluble in water (about 13–14 g./10 ml. H_2O at 18°C). Insoluble in alcohol and ether.

REFERENCE:

O. Olsson-Collenberg. Z. anorg. allg. Chem. 88, 50 (1914); H. Baadsgaard and W. D. Treadwell. Helv. Chim. Acta 38, 1669 (1955).

Potassium Octacyanotungstate (V)

$$K_3[W(CN)_8] \cdot H_2O$$

A solution of $K_4[W(CN)_8] \cdot 2\,H_2O$ (11.69 g. = 0.05 moles) in 125 ml. of water (acidified with 2 ml. of conc. HNO_3 and titrated with permanganate to a permanent red color) is prepared. The silver salt is then precipitated by addition of 0.21 g. (0.08 moles) of $AgNO_3$ dissolved in 50 ml. of water. The solid is washed with dil. HNO_3, dissolved in the minimum amount of ammonia, and reprecipitated with some dil. HNO_3. After thorough washing with water, the salt is suspended in 50 ml. of water and converted to the potassium salt by addition of 0.11 g. (0.07 moles) of KCl. The AgCl precipitate is removed by filtration, and the filtrate is treated with alcohol until the $K_3[W(CN)_8] \cdot H_2O$ precipitates. It is filtered and dried over $CaCl_2$. The yield can be as high as 91%, based on the starting tungstate (IV).

PROPERTIES:

Formula weight 527.4. Small lemon-yellow crystals, readily soluble in water.

REFERENCES:

O. Olsson-Collenberg. Z. anorg. allg. Chem. 88, 50 (1914); H. Baadsgard and W. D. Treadwell. Helv. Chim. Acta 38, 1669 (1955).

Uranium

U

The preparation of the pure metal is rendered difficult by its great tendency to combine with O, N, C, etc., and to alloy with many metals.

Basically, the following preparative methods are available:

a) Reduction of uranium oxides or halides with suitable metals, such as Na, Mg, Ca (methods I to IV).

b) Electrolysis (method V).

I. In the Jander method, UO_2 is reduced with metallic Ca:

$$\underset{270.1}{UO_2} + 2\,\underset{80.2}{Ca} = \underset{238.1}{U} + 2\,\underset{112.2}{CaO}$$

The reactor is an iron crucible about 13 cm. high, 1.6 cm. I.D., with a 0.1-cm. wall. This is charged with the reactant mixture, consisting of 7 g. of UO_2 and 11 g. of Ca turnings (the latter should be as freshly distilled as possible). The crucible cover is then welded on and the reactor heated for one hour at 1000–1100°C (the crucible should be embedded in charcoal powder to protect it from oxidation). The crucible is then completely cooled, opened, and the contents are covered with 90% alcohol saturated with NH_4Cl. Aqueous NH_4Cl solution is then added. The material is washed with water and then with alcohol. The product consists of four different fractions:

a) a very finely divided oxide-containing uranium, which can be separated by slurrying;

b) iron metal particles with a small uranium content, which can be removed after drying by means of a magnet;

c) nonmagnetic metal flakes (uranium with a high content of iron), which can be separated on a 140–170 U.S. standard sieve;

d) a very fine gray-brown powder, containing about 97% U and 2–3% Fe, but only very small amounts of O. The yield of this fraction is 66%.

The presence of iron impurity in the product can be avoided by coating the inner surface of the iron crucible with calcium carbonate, but the shrinkage of this lining during drying and its fragility necessitate considerable care in handling. A reactor lined with calcium carbonate is capable of producing material containing 99.9% U, although the yield is appreciably lower than in the above-described procedure.

II. Very pure uranium is obtained by reduction of U_3O_8 with freshly distilled Ca in high vacuum. The mixture is heated above

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the melting point of Ca, and the U is obtained as a fine gray powder which can be separated from the by-product CaO by sieving. Any unused Ca (which is present in excess) sublimes out from the product at the reaction temperature. The product analyzes as 99.95% U.

III. Both of the above procedures may be improved by adding to the reactant mixtures a mixture of scrupulously predried and prefused $CaCl_2$ and $BaCl_2$. The salt mixture serves as a flux and at high temperatures dissolves both the CaO and Ca metal. It is further recommended that the product be reduced a second time under the same conditions; this is because the first reduction normally goes to equilibrium and no further.

IV. Many variations of the reaction of uranium chlorides with metallic Na in sealed iron vessels have been described. The products range in purity from 99 to 100% U. The preparative method described below is based on the earlier procedures and attempts to overcome some of their shortcomings; however, it affords a uranium whose x-ray diffraction pattern still clearly shows UO_2 lines. For this reason one must question the assertions of earlier authors who claimed that this procedure gives a completely pure product.

$$\underset{379.9}{UCl_4} + \underset{92.0}{4\,Na} = \underset{238.1}{U} + 4\,NaCl$$

$$\underset{415.4}{UCl_5} + \underset{115.0}{5\,Na} = \underset{238.1}{U} + 5\,NaCl$$

An alumina tube closed at one end (a so-called Tammann crucible), 12 cm. high and 2 cm. I.D., is charged successively with 5 g. of NaCl, 13 g. of uranium chloride (for preparation, see p. 1436 under UCl_4, method I), and 4.5 g. of Na metal (freshly cut under ether). The materials must be added as rapidly as possible and then covered with NaCl up to 1 cm. below the top edge of the crucible. The filled tube is placed inside an only slightly larger iron crucible (3-mm. wall thickness) and the lid of the latter is welded on (see also Part III, Intermetallic Compounds, preparation of alloys by fusion of components). Two thick wires or bars are welded onto the outside of the iron crucible so that it may be suspended in a vertical tubular electric furnace. The reactor is gradually heated to 1150°C (2 hours), held for 15 minutes at this temperature, and then allowed to cool. The crucible is opened, and the contents of the alumina tube are treated with HCl-saturated methanol to remove unreacted Na, then with hot water to dissolve away the NaCl. Yellow $Na_2U_2O_7$ may appear

during this operation, even if the chloride reactant contained only a small percentage of UO_2Cl_2. However, the $Na_2U_2O_7$ may be separated completely from the U metal residue by repeated slurrying with water and decantation. The residue is then washed several times with HCl-saturated methanol and with water. Finally, light-gray metallic pellets are obtained.

V. ELECTROLYTIC PREPARATION

Very pure uranium is obtained by electrolysis of KUF_5 in an $NaCl$-$CaCl_2$ melt. A cylindrical graphite crucible serves both as the electrolysis vessel and the anode. It has an I.D. of 6 cm., a height of 15 cm. and walls 1-2 cm. thick. The electrical connection is made with a strip of Ni sheet wrapped around the upper part of the outside wall. The cathode is a strip of Mo sheet, 0.5 mm. thick and 1 cm. wide, which is immersed in the melt so that its lower end is 2.5 cm. above the bottom of the crucible. The latter stands in a suitable refractory vessel, around which a heating wire is wound. The entire apparatus is placed in a large-diameter lead vessel filled with thermal insulation.

A mixture of 250 g. of NaCl and 250 g. of anhydrous $CaCl_2$ is first fused together, and the melt temperature is adjusted as exactly as possible to 775°C. When the mixture is thoroughly melted, the cathode is inserted and the current is turned on (30 amp., potential drop between the electrodes about 5 v.). The current density should be 10 amp./in.^{2}.

Now, 30 g. of KUF_5 is added in small portions so that it melts as rapidly as possible. After addition of the KUF_5 is completed, a deposit of U begins to form on the cathode, where it appears in the form of a metallic tree; this reaches a thickness of about 2.5 cm. in 45 minutes. The old cathode is then slowly withdrawn from the melt, a new one is introduced, and the electrolysis is continued as before, while fresh salts are added to the melt as needed.

The material adhering to the cathode consists of a gray, spongy mass, which is permeated and surrounded by solidified melt. The melt protects the material from oxidation during cooling. After thorough cooling, the solids are stripped off the cathode and treated with water. Most of the salts dissolve quite easily, while the residue of heavy U powder can be readily and completely freed from traces of CaF_2, etc., by slurrying with water. The fraction consisting of very fine particles should be separated at the same time, since this material oxidizes very easily. The residue then comprises pure, fairly coarse particles of gray metal. The latter is washed with 5% acetic acid, followed by alcohol and ether; it is dried in vacuum and stored in air-tight vessels. This material is not pyrophoric. However, if the fine

metal powder is not removed the dry product may ignite in air under some circumstances.

PROPERTIES:

Light-gray pellets or black powder. M.p. 1689°; d 18.685. May be distilled using an electric furnace. Dissolves in dil. HCl and H_2SO_4 (slowly in cold acids but rapidly in warm ones), evolving H_2.

REFERENCES:

H. Funk. Darstellung der Metalle im Laboratorium [Preparation of Metals in the Laboratory], Stuttgart, 1938.
I. W. Jander. Z. anorg. allg. Chem. 138, 321 (1924).
II. E. Botolfsen. Bull. Soc. Chim. France 45, 626 (1929).
III. W. Kroll. Z. Metallkunde 28, 30 (1936).
IV. J. Zimmermann. Liebigs Ann. 216, 16 (1883); A. Fischer. Z. anorg. Chem. 81, 170 (1913); A. Roderburg. Ibid. 81, 122 (1913); D. Lely and L. Hamburger. Z. anorg. allg. Chem. 87, 220 (1914); H. Haag and G. Brauer. Data from the Chem. Lab. of the Univ. of Freiburg i. Br., 1950.
V. F. H. Driggs and W. C. Lilliendahl. Ind. Eng. Chem. 22, 516 (1930).

Uranium Hydride

UH_3

$$\underset{238.1}{U} + \underset{33.6\,l.}{3/2\,H_2} = \underset{241.1}{UH_3}$$

This procedure is successful only when very pure uranium metal is employed.

Uranium (10 g.) is freed of the adherent oxide layer by brief treatment with dil. nitric acid, washing with water, and drying over P_2O_5. The metal is then coarsely ground and placed in a porcelain boat, which should be large enough to accommodate the increase in volume which accompanies the hydride formation. Hydrogen is then passed over it at 250°C. [The pretreatment of the H_2 includes passage through a copper column heated to 650-700°C, a drying agent (magnesium perchlorate), and uranium powder heated to 700-750°C.] The reaction is complete after 20-30 minutes; the yield is quantitative.

See also Part II, Section I, p. 113 f.

PROPERTIES:

Fine, black, pyrophoric powder. Loses H_2 when heated in vacuum above 250°C, forming a uranium of high chemical activity. Powerful reducing agent; reacts vigorously with water according to: $2\ UH_3 + 4\ H_2O = 2\ UO_2 + 7\ H_2$.

REFERENCES:

F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, J. B. Johns and A. H. Daane, Nucleonics 4, 4 (1949).

Uranium (III) Chloride

UCl_3

$$UCl_4 + \tfrac{1}{2}H_2 = UCl_3 + HCl$$
$$379.9 \quad 11.2\ l. \quad 344.4 \quad 36.5$$

I. Completely pure UCl_4 is reduced with H_2 in the same tube in which it is prepared. The reduction proceeds below red heat and then at dull-red heat, until the off-gases are free of HCl. Absolutely pure H_2 must be used. The dull-brown, very hygroscopic UCl_3 adheres strongly to glass. Thus, when the mechanically separated product is dissolved, some brown to brick-red U (IV) silicate is always obtained as a residue.

II. Uranium is reacted with dry HCl at 250–300°C.

PROPERTIES:

Lustrous, dark-red, very hygroscopic needles; d_4^{25} 5.440. Very readily soluble in water, giving a purple-red liquid which becomes green within a few seconds as H_2 is evolved and a red precipitate forms. Insoluble in anhydrous alcohol, acetic acid, CCl_4, $CHCl_3$, acetone and pyridine.

REFERENCES:

I. A. Rosenheim and H. Leobel. Z. anorg. Chem. 57, 235 (1908); W. Biltz and C. Fendius. Z. anorg. allg. Chem. 172, 386 (1928); J. F. Suttle in: Th. Moeller, Inorg. Syntheses, Vol. V, New York–Toronto–London, 1957, p. 145.
II. E. Staritzky. Analyt. Chem. 28, 1055 (1956).

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Uranium (IV) Chloride

UCl_4

I. The preparation of completely pure UCl_4 (or UCl_5) is difficult since under normal conditions there exists an equilibrium: $2\ UCl_4 + Cl_2 = 2\ UCl_5$. However, for many purposes, especially for the subsequent reduction to metallic U, any mixture of the two uranium chlorides is adequate. Such a mixture is prepared rapidly and conveniently by the following method.

$$\underset{270.1}{UO_2} + \underset{12.0}{C} + 2\tfrac{1}{2}Cl_2\ (2\,Cl_2) = \underset{415.4}{UCl_5}\ (\underset{379.9}{UCl_4}) + CO_2$$

A quartz tube 40 cm. long and 2 cm. I.D., both ends of which carry ground joints, is charged with a mixture of 20 g. of UO_2 and 7 g. of carbon black, distributed along the entire length of the tube. One end of the reactor tube is connected to a wash bottle containing H_2SO_4; the latter, in turn, is connected to a U tube filled with P_2O_5, which is attached to a Cl_2 cylinder. The other end of the reactor is connected to two ground-joint Erlenmeyer flasks in series (do not use round-bottom flasks; these are not as well suited for the precipitation operation), which in turn are attached to a wash bottle with H_2SO_4 (the latter is connected backward and serves as a trap for atmospheric moisture). All joints are lubricated with vitreous phosphoric acid. A very fast stream of Cl_2 is passed through this apparatus. When all the air is displaced, the reactor is heated with two rosette burners, beginning at the Cl_2 inlet. Within a short time the uranium chloride begins to sublime into the cooler part of the tube, largely as a brown vapor. By shifting the burners to the next zone of the tube as the reaction is completed in the preceding one, it is possible to sublime most of the uranium chloride into the two Erlenmeyer flasks. The yield is almost quantitative. It takes one hour to obtain about 13 g. of uranium chloride from 20 g. of UO_2.

Chlorination of U_3O_8 under identical conditions, sometimes recommended in the literature, gives chlorides greatly contaminated with UO_2Cl_2.

II. UCl_4 may be obtained by heating a mixture of 20 g. of UO_2 and about 6 g. of sugar-derived charcoal, covered with some additional sugar charcoal powder. The reactants are in an unglazed boat and a stream of Cl_2 is passed over the latter (the air is first displaced by evacuation and several purgings with Cl_2). The reaction begins at 450°C and is completed at 600–700°C. The UCl_4 is driven into a spherical receiver sealed onto the reactor tube to decompose the by-product UCl_5. The material must be redistilled in a CO_2 stream into a second receiver sealed onto the first.

III.

$$\underset{270.1}{UO_2} + 2\,\underset{237.9}{SOCl_2} = \underset{379.9}{UCl_4} + 2\,\underset{128.1}{SO_2}$$

A bomb tube of ~ 1.5 cm. I.D. is charged with 5.6 g. of pure UO_2 and 10 ml. of $SOCl_2$ (freshly distilled in vacuum); these are then thoroughly mixed. The sealed tube is heated for 7 days at 200°C; the time required for completion of the reaction may be somewhat reduced if the tube is briefly cooled at regular intervals and the SO_2 formed is permitted to escape.

The product consists of UCl_4, partially dissolved in $SOCl_2$ and partially present as green crystals. The lower part of the bomb tube is cut off, the entire contents rinsed rapidly with some $SOCl_2$ into a 100-ml. ground-joint flask and distilled under reduced pressure (e.g., 140 mm.) in a stream of dry N_2 (or CO_2) to remove the $SOCl_2$. Finally, the brown adduct of $SOCl_2$ and UCl_4 is decomposed by heating at about 150°C until a pure green residue of UCl_4 is obtained (half an hour is required). Yield: about 7.5 g. (95%).

IV. Analogous to Hönigschmid's method for UBr_4 (see p. 1440 f.). The product has the composition indicated by the formula. The procedure is somewhat tedious because of numerous precautionary measures necessary. Useful only for small quantities.

DropBooks

V. Chlorination of UCl_3 at 250°C.

PROPERTIES:

Formula weight 379.90. Light-green needles or dark-green octahedra, which sublime at red heat as a red vapor. M.p. 567°, b.p. 618°; d_4^{25} 4.73–4.97. The aqueous solution gives a strongly acidic reaction because of hydrolysis. Soluble in ethyl acetate and benzoate; insoluble in ether, chloroform and benzene.

REFERENCES:

I. H. Haag and G. Brauer. Experiments at chemical laboratories of the University of Freiburg i. Br., 1950.

II. A. Voigt and W. Biltz. Z. anorg. allg. Chem. 133, 281 (1924).

III. H. Hecht, G. Jander and H. Schlapmann. Ibid. 254, 255 (1947); checked at chemical laboratories of the University of Freiburg i. Br., 1951.

IV. O. Hönigschmid and W. E. Schilz. Z. anorg. allg. Chem. 170, 148 (1928); O. Hönigschmid and F. Wittner. Ibid. 226, 296 (1936).

V. E. Staritzky. Analyt. Chem. 28, 1056 (1956). See also J. A. Hermann and J. F. Suttle in: Th. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 143.

Uranium (V) Chloride

UCl_5

$$UCl_4 + \tfrac{1}{2}Cl_2 = UCl_5$$
$$379.9 \quad 11.0\,l. \quad 415.4$$

A very clean hard-glass tube *a–h*, bent as shown in Fig. 324, is charged at location *b* with a mixture of UCl_4 and finely divided wood charcoal, and attached immediately to a Cl_2-generating apparatus via joint *a*. The reactants and the glass tube are carefully dried by heating in the Cl_2 stream, which is predried over P_2O_5. When stronger heating is applied at *b*, a mixture of UCl_4 and UCl_5 distills toward *d*. To completely convert this chloride mixture into UCl_5, a sufficient quantity of Cl_2 is first frozen in *f* by cooling the latter; the tube is then sealed off at *c* and (after evacuation via joint *h*) at *g*. The solid Cl_2 at *f* is brought to 0°C. This results in a vapor pressure of about 3.6 atm. Then heating the tip of tube *d* causes sublimation of pure UCl_5 from the heated zone; it forms a dark-brown deposit at *e*.

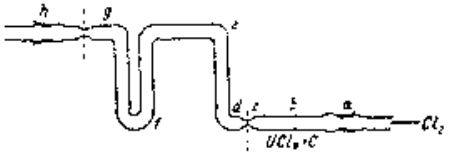

Fig. 324. Preparation of uranium (V) chloride.

Alternate method: Chlorination of U_3O_8 with CCl_4 in a sealed tube at 250°C (Michael and Murphy).

PROPERTIES:

Deep-brown, crystalline, very hygroscopic sublimate. Dissociates slowly, even at room temperature, to UCl_4 and Cl_2 (equilibrium partial pressure of Cl_2 at 20°C is at least 10^{-3} mm.); must therefore be stored in sealed vessels filled with Cl_2. Soluble in water with fizzing and evolution of HCl; soluble in absolute alcohol and acetone; the best solvents are ethyl acetate and benzonitrile.

REFERENCES:

H. Martin and K. H. Eidau, Z. anorg. allg. Chem. 251, 295 (1943); O. Ruff and A. Heinzelmann, Ber. dtsch. chem. Ges. 42, 495 (1909); A. Michael and A. Murphy, J. Amer. Chem. Soc. 44, 365 (1910).

Uranyl Chloride

UO_2Cl_2

$$\underset{420.2}{UO_2SO_4 \cdot 3\,H_2O} + \underset{208.3}{BaCl_2} = \underset{341.0}{UO_2Cl_2} + BaSO_4 + 3\,H_2O$$

$$\underset{286.1}{UO_3} + \underset{72.9}{2\,HCl} = \underset{341.0}{UO_2Cl_2} + H_2O$$

$$\underset{842.2}{U_3O_8} + \underset{218.8}{6\,HCl} + \underset{34.0}{H_2O_2} = \underset{1023.0}{3\,UO_2Cl_2} + 4\,H_2O$$

An aqueous solution of uranyl chloride is prepared by (*a*) dropwise addition of a $BaCl_2$ solution to a conc. solution of $UO_2SO_4 \cdot 3\,H_2O$ [for preparation, see p. 1447 under uranium (IV) sulfate] until all of the SO_4^{2-} ion is precipitated (no excess of $BaCl_2$), followed by filtration; or (*b*) by thoroughly boiling UO_3 with water to give a yellow powder of H_2UO_4, which is then dissolved in dil. HCl; or (*c*) by slurrying U_3O_8 in conc. HCl, followed by dropwise addition of 30% H_2O_2; the U_3O_8 is thus dissolved as UO_2Cl_2, although the reaction is slow.

Careful evaporation of any of the UO_2Cl_2 solutions on a water bath and then in a vacuum desiccator over conc. H_2SO_4 affords a crystalline mass of composition $UO_2Cl_2 \cdot H_2O$. To obtain $UO_2Cl_2 \cdot 3\,H_2O$, a small portion of the residue is heated with some conc. HCl, the resulting solution is allowed to evaporate in a desiccator, and the small crystals which separate are added to a conc. solution of the main body of the monohydrate, whereupon they grow into large, uniform prismatic crystals.

The $UO_2Cl_2 \cdot H_2O$ and $UO_2Cl_2 \cdot 3\,H_2O$ can be dehydrated without decomposition by the following method. The uranyl chloride is first dried over P_2O_5, placed in flat porcelain boats, and slowly heated in a dry HCl/Cl_2 stream to about 450°C over a period of 4–5 hours. Under these conditions no decomposition to the oxide takes place and only the water of crystallization is removed. If any $UO_2(OH)Cl$ is present, it is converted to UO_2Cl_2 by reaction with the HCl, liberating water.

Alternate methods: a) repeated evaporation of uranyl nitrate or acetate with conc. HCl yields UO_2Cl_2 solutions, which are crystallized in a vacuum desiccator over KOH. The amount of water of crystallization present in the product depends on the duration of the drying period.

b) Oxidation of UCl_4 with O_2 (Leary and Suttle).

PROPERTIES:

UO_2Cl_2

Golden-yellow when completely anhydrous; hydrated UO_2Cl_2 exhibits a greenish luster.

$UO_2Cl_2 \cdot 3\ H_2O$

Formula weight 395.03. Yellow-green, fluorescent, oblique-angled prisms, deliquescent in air; extremely soluble in water, alcohol and ether. At 18°C, 7.35 wt. parts of $UO_2Cl_2 \cdot 3\ H_2O$ dissolve in 1 part of H_2O; the saturated solution is very viscous.

REFERENCES:

F. Mylius and R. Dietz. Ber. dtsch. chem. Ges. 34, 2774 (1901); W. Oechsner de Coninck. Comptes Rendus Hebd. Séances Acad. Sci. 148, 1769 (1909); L. Ochs and F. Strassmann. Z. Naturforsch. 7 b, 637 (1952); H. A. Leary and J. F. Suttle in: Th. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 148.

Uranium (IV) Bromide

UBr_4

Prepared by brominating a mixture of UO_2 and charcoal.

The apparatus used by Hönigschmid (Fig. 325) consists essentially of two parts: the glass section *A* and the quartz tube *B* with receiver *C*. Section *A* serves to hold the weighing tube and its stopper, and is attached to the quartz tube *B* by means of a large flange joint. Section *B* has a sacklike protuberance on one side, of the same I.D. as the quartz tube itself.

System *D*, comprising 3 quartz tubes connected by ground joints, is inserted into tube *B*. The side view of this system is shown separately in the figure, and is also reproduced in the main drawing. Tube *a-d*, constricted in the middle, carries a quartz boat containing the oxide-charcoal mixture. Tube *b*, which will be stored later in the weighing tube mentioned above, serves as a receiver for the pure, fused UBr_4. Tube *c* leads the uncondensed bromide vapors into the receiver.

The quartz boat is charged with a mixture of 1 part of sugar-derived charcoal and 4 parts of uranium oxide, intimately ground together in an agate mortar. The boat is then inserted into tube *a*. The flanged joint and all stopcocks which will come in contact with bromine vapor are greased with sirupy metaphosphoric acid. The flanged connection is held together with strong metal springs. The apparatus is heated with small electric tube furnaces which can be shifted along the length of the quartz tube as far as the protuberance.

The apparatus is first filled with N_2, and the quartz tube is heated along its entire length (beginning at the protuberance) in order to dry the material. Then a Br_2-saturated stream of N_2 is

introduced and the furnaces are shifted in such a manner that the entire system of tubes can be heated as far as part *d*. The temperature is raised to yellow heat; the UBr_4 begins to form and condenses in *d*. Tubes *b* and *c* remain completely free of material and only a small amount of UBr_4 collects in receiver *C*. About 5 g. of UBr_4 forms in one hour. The furnaces are now shifted in such a way that the preweighed tube *b* remains cold, yet the sublimate in *d* is heated to yellow heat. The second sublimation (from *d* into *b*) is carried out either in bromine vapor or in pure N_2.

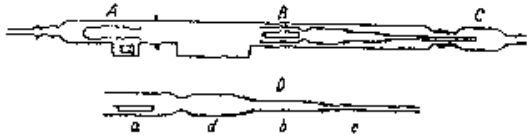

Fig. 325. Preparation of uranium (IV) bromide.

The melting of the UBr_4 should be accomplished without a loss, if possible, and without too long an exposure to high temperature. Thus, after completion of the sublimation, the entire system of tubes is pushed toward the protuberance by means of a quartz rod inserted through receiver *C*, while all furnaces are still at their maximum temperature. In this way the small tube *b* with the UBr_4 is shifted into the hottest part of the apparatus. The sublimate fuses in a few moments; the furnaces are now shut down and removed at once. Unnecessary overheating of the UBr_4 is thus avoided.

The apparatus is allowed to cool in a stream of N_2, and are then filled with dry air. In disassembling the tube system, receiver *C* is removed first and the individual joints are loosened with a long glass rod provided with a small hook, while a steady, fast stream of air is passed through. Tube *a* is pushed up to the protuberance and is allowed to glide into the latter by gently turning the whole apparatus. Then tube *b* with the fused sublimate is pushed into the previously prepared weighing tube, which is then closed in the usual manner. The length of the run from the beginning of heating to the disassembly of the apparatus is 3 hours or less.

PROPERTIES:

Formula weight 557.73. d^{21}_4 4.838. Lustrous, brown to black leaflets, sublimable in a Br_2-N_2 stream; in N_2 alone, dissociates partially to UBr_3 and Br_2. Dissolves in H_2O with fizzing and formation of a green liquid.

REFERENCES:

O. Hönigschmid. Monatsh. Chem. 36, 59 (1915); O. Hönigschmid and F. Wittner. Z. anorg. allg. Chem. 226, 296 (1936).

Uranium (IV) Oxide

UO_2

I. $$\underset{842.2}{U_3O_8} + \underset{44.81.}{2\,H_2} = \underset{810.2}{3\,UO_2} + \underset{36.0}{2\,H_2O}$$

The starting U_3O_8 is prepared by heating pure uranyl nitrate, oxalate or peroxide (or ammonium diuranate) to 700–800°C; it is then reduced with H_2 at 900°C and allowed to cool in the stream of H_2.

II. $$\underset{412.1}{UO_2C_2O_4 \cdot 3\,H_2O} = \underset{270.1}{UO_2} + 2\,CO_2 + 3\,H_2O$$

Precipitation of a hot conc. solution of uranyl nitrate with oxalic acid yields a yellow powder of $UO_2C_2O_4 \cdot 3\,H_2O$; this is converted to black, very fine, pyrophoric UO_2 powder in a stream of H_2 even below red heat.

REFERENCES:

Formula weight 270.1. Brown powder. M.p. 2176° under N_2; d_4^{25} 10.8. Crystal structure: C 1 (fluorite) type.

REFERENCES:

I. W. Biltz and H. Müller, Z. anorg. allg. Chem. 163, 261 (1927).
II. W. Jander. Ibid. 138, 321 (1924).

Uranium (VI) Oxide

UO_3

Pure UO_3 is difficult to prepare because the thermal cleavage of uranyl compounds does not free the product of traces of volatile components, while at high temperatures dissociation into U_3O_8 and O_2 becomes objectionable. To circumvent these drawbacks it is desirable to use O_2 at a pressure above atmospheric.

I. $$\underset{338.1}{UO_4 \cdot 2\,H_2O} = \underset{286.1}{UO_3} + {}^1/_2O_2 + 2\,H_2O$$

A weighing tube is charged with 5–10 g. of the dry peroxide and placed (unstoppered) in an electric crucible furnace preheated to 350°C. A fast stream of O_2 is admitted through the opening in the

furnace lid. The temperature is initially held for 3–5 hours at 350°C and then for one half to one hour at 400°C. The weighing tube is then stoppered and allowed to cool in a desiccator.

II. Uranyl nitrate is heated in O_2 to 500°C; however, the product still contains traces of water.

III. $$\underset{842.2}{U_3O_8} + {}^1/_2O_2 = 3\,\underset{858.2}{UO_3}$$

Figure 326 shows the apparatus in which rather large quantities of U_3O_8 can be converted to UO_3 at an oxygen pressure higher than atmospheric. The reactor r consists of an Inconel (a Cr–Ni alloy) tube which is screwed into a brass flange plate. This plate also carries a seal seat groove with a neoprene gasket. The upper, blind flange plate, also made of brass, carries the seal tongue and is drilled for a welded-on brass cross. The latter is connected to two high-pressure diaphragm valves and a pressure gage. A removable quartz insert q facilitates replacement of reactants. Manometer m is arranged in such a way that it also serves as a pressure-relief valve. The graduated tube g is for the liquid oxygen; it must contain sufficient oxygen to generate the desired pressure in the reactor.

Pure U_3O_8 (or UO_3 prepared as in method I) is placed in the quartz insert tube g and the reactor assembled to the flanges. The entire system is purged with O_2, beginning at stopcock h_1; the O_2 may be discharged at the pressure gage. Then stopcock h_1 is closed and the apparatus is evacuated by opening stopcocks h_2 and h_3; in this operation, valve v_4 is open and v_5 closed. The U_3O_8 is completely dried by heating reactor r for one hour at 850°C while maintaining the vacuum. A McLeod gage is used to ascertain when the apparatus is completely evacuated; the vacuum connection at stopcock h_2 is then closed, as are stopcock h_3 and valve v_4. Trap f is filled with liquid O_2 by immersing it in liquid N_2 and opening h_1. The amount of O_2 condensed in the trap should exceed by 10% that required to bring the pressure in the reactor to 27 atm. gage. This O_2 quantity can be estimated more exactly after the apparatus has been used once. When sufficient O_2 is condensed in the trap, stopcock h_1 is closed. Now the graduated tube g is immersed in a Dewar flask filled with liquid N_2 and stopcock h_3 is opened. The exact quantity of O_2 which is needed to attain the required gage pressure is measured into g and stopcock h_3 is then closed. The reactor is cooled in liquid N_2 and valve v_4 is opened. Tube g is then immersed in liquid O_2 in order to establish an inside pressure of about 1 atm.; this causes the O_2 to distill over into the reactor. Next, valve v_4 is closed and the reactor r is brought very gradually to room temperature in order to avoid scattering of the U_3O_8 by

the evaporating O_2. The best procedure for doing this is to replace the liquid-N_2-filled Dewar flask with an empty one. The reactor tube is placed in an electric furnace and heated for 40 hours at 600–700°C. If too much O_2 is condensed in the reactor, the excess can be discharged through valve v_3. The liquid O_2 remaining in trap f can be removed by vacuum, or allowed to escape (slowly) through the manometer while the trap is in a Dewar flask containing gradually evaporating liquid N_2.

According to x-ray diffraction data, this procedure yields pure UO_3.

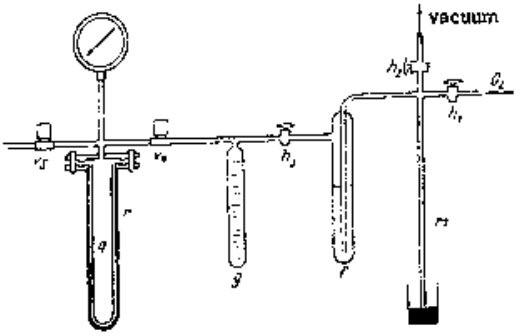

Fig. 326. Preparation of uranium (VI) oxide. r Inconel reactor; q quartz insert tube; g graduated condensation trap; f condensation trap; m manometer and pressure-relief valve; v valves.

PROPERTIES:

Bright orange-yellow, very hygroscopic, amorphous powder or hexagonal crystals; d_4^{25} 7.368. Soluble in mineral acids, forming uranyl salts. In water, it hydrates in 24 hours at room temperature to give $UO_3 \cdot H_2O$.

A red, hexagonal modification, which is less stable, forms at 450–500°C; its crystal structure resembles that of U_3O_8.

REFERENCES:

I. W. Biltz and H. Müller. Z. anorg. allg. Chem. 163, 258 (1927).
II. G. F. Hüttig and E. v. Schroeder. Ibid. 121, 250 (1922); S. S. Lu. Sci. Technol. China 1, 12 (1948), abstr. in Chem. Zentr. 1949, II, 951.
III. J. Sheft, S. Fried and N. Davidson. J. Amer. Chem. Soc. 72, 2172 (1950).

Alkali Uranates (VI)

Li_2UO_4, Na_2UO_4, K_2UO_4

$$\underset{286.1}{UO_3} + \underset{73.9\ \ (106.0,\ \ 138.2)}{Li_2CO_3(Na_2CO_3, K_2CO_3)} = \underset{315.0\ \ (348.1,\ \ 380.3)}{Li_2UO_4(Na_2UO_4, K_2UO_4)} + \underset{}{CO_2}$$

Alkali carbonate and UO_3 (1:1 mole ratio) are intimately ground, placed in a large-diameter crucible, and gradually heated in an electric furnace to 800°C while O_2 is slowly passed through. The process is interrupted several times to regrind the reactants. The end of the reaction is recognized by the failure of a sample to evolve CO_2 on dissolution in dil. hydrochloric acid (2–3 days required to reach this point).

PROPERTIES:

Light orange when finely divided. Aqueous slurries show a distinctly alkaline reaction within a few minutes. Soluble in dilute hydrochloric acid and sulfuric acid, as well as in 2 N acetic acid (except for potassium uranate).

REFERENCE:

W. Rüdorff and H. Leutner. Z. anorg. allg. Chem. 292, 193 (1957).

DropBooks

Alkali Uranates (V)

$LiUO_3$, $NaUO_3$

$$\underset{315.9\ \ (348.0)}{Li_2UO_4(Na_2UO_4)} + \underset{270.1}{UO_2} = 2\,\underset{586.0\ \ (618.1)}{LiUO_3(NaUO_3)}$$

A mixture of alkali uranate (VI) and UO_2 (1:1 mole ratio) is heated in evacuated, sealed quartz ampoules at 650–750°C. The ampoules are opened at intervals of 10–20 hours, the reaction product is reground to a fine powder, and the heating is resumed using a new ampoule. The reaction is complete in 75–100 hours; the lithium compound forms in a somewhat shorter time and at a somewhat lower temperature.

PROPERTIES:

Formula weights: $LiUO_3$ 293.0; $NaUO_3$ 309.1. $LiUO_3$ is dark violet, $NaUO_3$ brown-violet. Both are very stable. Much more resistant to acids than the corresponding uranates (VI). Dilute hydrochloric and sulfuric acids have no effect in the cold. Dissolve in dil. nitric acid.

REFERENCE:

W. Rüdorff and H. Leutner. Z. anorg. allg. Chem. 292, 193 (1957).

Uranium Peroxide

$UO_4 \cdot 2H_2O$

Precipitates from uranyl nitrate solutions on addition of H_2O_2.

I. A boiling 10% solution of uranyl nitrate is treated dropwise with 30% H_2O_2. The resulting amorphous, white precipitate is filtered on the finest filter possible (membrane or Millipore filter) and washed thoroughly with boiling water. The peroxide, which is a bright sulfur-yellow after filtration, is first dried in the air on a clay plate, then at 100°C to constant weight, and stored in vacuum over P_2O_5.

II. Reaction of $(NH_4)_2[UO_2(C_2O_4)_2] \cdot 3\ H_2O$ with H_2O_2 yields crystalline, nonhygroscopic $UO_4 \cdot 3\ H_2O$, which is converted to the dihydrate by storing in vacuum over P_2O_5.

III. A readily filterable peroxide hydrate is obtained from the reaction of 50 ml. of 30% H_2O_2 with 3 g. of UO_3 (half a day at room temperature).

PROPERTIES:

Formula weight of $UO_4 \cdot 2\ H_2O$: 338.10. Yellowish-white, amorphous powder or fine needles.

REFERENCES:

I and II. A. Rosenheim and H. Daehr. Z. anorg. allg. Chem. 181, 178, 180 (1929).
III. A. Sieverts and E. Müller. Ibid. 173, 299 (1928).

Uranium (IV) Sulfide

US_2

$$\underset{379.9}{UCl_4} + \underset{44.81.}{2\,H_2S} = \underset{302.2}{US_2} + 4\,HCl$$

I. The best starting material for the preparation of US_2 is Na_2UCl_6; this material is preferable to UCl_4 because its volatility is lower.

The starting mixture is prepared during the synthesis of UCl_4 (see p. 1436, method II); thus, the sealed-on round receiving flask is precharged with 10 g. of ignited NaCl. Fusion of the UCl_4 with NaCl yields a green cake. The Cl_2 is removed by evacuation of the reactor tube. Then a stream of dry H_2S (either generated from the liquefied material or made by passing pure, dry H_2 over a boat containing molten S) is passed over the Na_2UCl_6 while heating the latter to 600-700°C; the reaction is continued for 4–5 hours until the off-gases are free of HCl. The US_2 is allowed to cool under H_2S and washed briefly with deaerated ice water, then with alcohol and ether, and dried in vacuum at 140°C.

II. Prepared from U_3O_8 and H_2S at 1150°C (electric furnace); depending on the reaction conditions, either α- or β-US_2 is formed.

PROPERTIES:

Black leaflets with a metallic luster, altered only by prolonged standing in air; d_4^{25} 7.96.

REFERENCES:

DropBooks

I. E. F. Strotzer, O. Schneider and W. Biltz, Z. anorg. allg. Chem. 243, 307 (1940); A. Colani, Ann. Chim. Phys. (8) 12, 80 (1907); R. Flatt and W. Hess, Helv. Chim. Acta 21, 526 (1938).
II. M. Picon and J. Flahaut, Comptes Rendus Hebd. Séances Acad. Sci. 237, 808 (1953).

Uranium (IV) Sulfate

$U(SO_4)_2 \cdot 8\,H_2O$ or $4\,H_2O$

Prepared by cathodic reduction of UO_2SO_4:

$$\underset{(\cdot 3\,H_2O)\ 420.2}{UO_2SO_4} + \underset{98.1}{H_2SO_4} + 2e \longrightarrow \underset{(\cdot 8\,H_2O)\ 574.3}{U(SO_4)_2}$$

The electrolyte consists of an approximately saturated solution of $UO_2(SO_4) \cdot 3\,H_2O$ (1 mole) in about twice the stoichiometric quantity (2 moles) of H_2SO_4. The $UO_2SO_4 \cdot 3\,H_2O$ is prepared from $UO_2(NO_3)_2 \cdot 6\,H_2O$ by evaporating to dryness with H_2SO_4 and concentrating an aqueous solution of the residue to a sirupy consistency, whereupon the $UO_2SO_4 \cdot 3\,H_2O$ slowly crystallizes. The

UO_2SO_4-H_2SO_4 solution is placed in a cooled glass cylinder which houses the cathode space. A clay cell contains the anode. The best results are obtained with an Hg cathode and a carbon rod anode. The Hg layer is placed on the bottom of the cathode vessel; the electrical connection is made with a copper wire sealed into a glass tube. The reaction proceeds quite rapidly at 3-5 amp. Any material which separates during the electrolysis is redissolved by addition of some water. At the end the cathode liquid becomes dark green with a steel-blue to black-violet fluorescence. If the electrolysis continues beyond the tetravalent state, the reddish brown color (in transmitted light) of trivalent uranium becomes apparent; however, this compound is very unstable and is quickly reoxidized in air to tetravalent uranium.

The concentrated acidic $U(SO_4)_2$ solution thus obtained is very stable and may be kept for weeks, in contrast to the very dilute solution.

Concentration of the solution in vacuum over H_2SO_4 yields $U(SO_4)_2 \cdot 8\ H_2O$ as large, dark-green crystals; alternately, the product may be obtained by evaporation in air below 75°C. If the product is precipitated with alcohol in the cold, it is a light-green, fine crystalline powder.

The tetrahydrate $U(SO_4)_2 \cdot 4H_2O$ is prepared by dropwise addition of conc. H_2SO_4 to the reduced solution (high-speed stirring); the H_2SO_4 is added until no further precipitation occurs. During this operation the temperature rises to 40-50°C.

The salt is washed with alcohol and ether and dried on a clay plate.

PROPERTIES:

$U(SO_4)_2 \cdot 8\ H_4O$: Formula weight 574.32. Dark-green monoclinic prismatic crystals. Hydrolyzes on solution in water, precipitating the basic sulfate $UOSO_4 \cdot 2\ H_2O$. Solubility (20°C): 8.78 g./100 g. of solution in 0.1 N H_2SO_4.

$U(SO_4)_2 \cdot 4\ H_2O$: Formula weight 502.26. Whitish-green precipitate composed of needles arranged in a starlike form. Soluble in water with separation of the basic sulfate; soluble in dilute acids.

REFERENCE:

R. J. Meyer and H. Nachod. Liebigs Ann. 440, 186 (1924).

Ammonium Uranyl Carbonate

$$(NH_4)_4[UO_2(CO_3)_3]$$

$$\underset{(\cdot 6\,H_2O)\ 1004.4}{2\,UO_2(NO_3)_2} + 6\,NH_3 + 3\,H_2O = \underset{624.2}{(NH_4)_2U_2O_7} + 4\,NH_4NO_3$$

$$\underset{624.2}{(NH_4)_2U_2O_7} + 6\,(NH_4)_2CO_3 = \underset{1044.5}{2\,(NH_4)_4[UO_2(CO_3)_3]} + 6\,NH_3 + 3\,H_2O$$

The $(NH_4)_2U_2O_7$ is precipitated from an aqueous solution of 10 g. of $UO_2(NO_3)_2 \cdot 6\,H_2O$ by addition of conc. ammonia. The fine yellow powder is suction-filtered, washed with water, and stirred with an excess of conc. $(NH_4)_2CO_3$ solution for about 10 minutes (the flask is on a 70°C water bath). The clear supernatant liquid is decanted and allowed to stand overnight. Yellow crystals precipitate; these are filtered with suction and dried in air. The residue of undissolved $(NH_4)_2U_2O_7$ is treated several times with the mother liquor at 70°C, as described above, until crystals no longer form on cooling. Yield: 5–8 g.

PROPERTIES:

Formula weight 522.26. Well-formed, transparent yellow crystals, monoclinic prismatic; d 2.773. Sparingly soluble in water; insoluble in alcohol and ether; may be recrystallized without decomposition from aqueous $(NH_4)_2CO_3$.

DropBooks

REFERENCE:

Ebelmen, Liebigs Ann. 43, 302 (1842).

Uranium (IV) Oxalate

$$U(C_2O_4)_2 \cdot 6\,H_2O$$

$$\underset{(2\,H_2O)\ 424.2}{UO_2(CH_3COO)_2} + 4\,HCl + \underset{(\cdot 2\,H_2O)\ 210.1}{Na_2S_2O_4} = UCl_4 + 2\,NaHSO_3 + 2\,CH_3COOH$$

$$\underset{180.1}{UCl_4} + 2\,H_2C_2O_4 + 6\,H_2O = \underset{523.2}{U(C_2O_4)_2 \cdot 6\,H_2O} + 4\,HCl$$

Five grams (0.012 moles) of $UO_2(CH_3COO)_2 \cdot 2\,H_2O$ powder is dissolved in 100 ml. of dilute HCl (1 : 10 in water) preheated to 80°C. While stirring, 5 g. (0.024 moles) of $Na_2S_2O_4 \cdot 2\,H_2O$ powder is

added in small portions. The initial precipitate is brown, but rapidly changes to whitish-green. Then 5 ml. of conc. HCl is added and the mixture is heated for about 10 minutes on the water bath (until solution is complete). The dark-green solution of uranium (IV) salt is usually somewhat cloudy because of a haze of fine sulfur. It is filtered in the absence of air and treated while still warm (appr. 60°C) with a saturated oxalic acid solution; the latter is added slowly (good stirring). A heavy, solid gray precipitate forms at once. It settles in a few minutes and, after standing for one half hour, exhibits the dark-green color of uranium (IV) oxalate. It is washed 5 times with 100-ml. portions of water. Sulfite and oxalate should be removed completely by this operation. Since uranium (IV) oxalate is completely stable in air, it may be air dried. The yield is almost quantitative (5.7 g.).

PROPERTIES:

Dark-green microcrystals, stable in air [in contrast to solutions of uranium (IV) salts]. May be recrystallized from warm conc. hydrochloric acid. Only slightly soluble in water and dil. acids. Loses 5 moles of H_2O at 110°C, but the sixth mole only at about 200°C.

REFERENCES:

V. Kohlschütter and H. Rossi. Ber. dtsch. chem. Ges. 34, 1473, 3630 (1901); E. Marchi in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 166.

Potassium Tetraoxalatouranate (IV)

$$K_4[U(C_2O_4)_4] \cdot 5\,H_2O$$

$$\underset{522.2}{U(C_2O_4)_2 \cdot 6\,H_2O} + 2\,\underset{368.5}{K_2C_2O_4 \cdot H_2O} = \underset{836.6}{K_4[U(C_2O_4)_4] \cdot 5\,H_2O} + 3\,H_2O$$

A slurry of 6 g. (0.014 moles) of $U(C_2O_4) \cdot 6\,H_2O$ in 50 ml. of water is treated in the absence of air with a solution of 5 g. (0.027 moles) of $K_2C_2O_4 \cdot H_2O$ in 20 ml. of water and allowed to stand on a steam bath for one hour. It is then filtered and the dark-green filtrate is treated dropwise with 200 ml. of absolute alcohol (good stirring). Small light-green crystals precipitate. These are filtered off, washed with absolute alcohol, then with ether, and dried over P_2O_5.

PROPERTIES:

Readily soluble in water (21.7 g. per 100 g. of water at 17°C), but only very slightly soluble in water–alcohol mixtures. Converted to the monohydrate by heating for a few hours at 200°C.

REFERENCES:

V. Kohlschütter. Ber. dtsch. chem. Ges. 34, 1472, 2619 (1901); E. Marchi in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York–Toronto–London, 1950, p. 169.

Uranium (V) Ethoxide

$$U(OC_2H_5)_5$$

$$UCl_4 + 4\,NaOC_2H_5 = U(OC_2H_5)_4 + 4\,NaCl$$

$$U(OC_2H_5)_4 + {}^1/_2\,Br_2 = U(OC_2H_5)_4Br$$

$$U(OC_2H_5)_4Br + NaOC_2H_5 = U(OC_2H_5)_5 + NaBr$$

A sodium ethoxide solution is prepared from 800 ml. of absolute ethanol and 46 g. (2 g.-atoms) of Na (use a 1-liter, three-neck flask). Toward the end of the reaction, refluxing and good stirring are needed. The solution is cooled to room temperature. Then, while stirring rapidly, 190 g. (0.5 moles) of fine UCl_4 powder is added in portions of about 20 g. (5-minute intervals). The contents of the flask are protected at all times against atmospheric moisture by means of a $CaCl_2$ tube. The heat of reaction causes the alcohol to boil, and the flask is therefore set in cold water. When all the UCl_4 has been added and the reaction subsides, the flask contents are refluxed on a steam bath for two hours (stirring). They are then cooled to room temperature and a solution of 40 g. (0.5 g.-atoms) of bromine in 20 ml. of dry benzene is added dropwise (rapid stirring) over a period of 15 minutes. The color changes from light green to brown, then gray and, toward the end of the addition, dark green.

While continuing the stirring, a sodium ethoxide solution prepared from 11.5 g. (0.5 g.-atoms) of Na in 200 ml. of absolute alcohol is rapidly added, causing the color to turn brown. The mixture is then distilled under anhydrous conditions to remove the alcohol. To achieve this, about one third of the material is introduced as rapidly as possible into a 500-ml. Claisen flask and the alcohol is distilled off on an oil bath (good stirring). Then the second fraction is added, etc. When the mass becomes solid, the stirrer is removed; the flask is closed off with a stopper and gradually heated to 150°C at 2–3 mm. The completely dry residue, which contains NaCl and $U(OC_2H_5)_5$, is now heated further on an oil bath at a vacuum of 0.001–0.004 mm. The uranium (V) ethoxide distills at a bath temperature of about 180–240°C. The yield may be as high as 217 g. (94%).

SYNONYM:

Uranium (V) ethylate.

PROPERTIES:

Dark-brown liquid. B.p. about 123°C at 0.001 mm.; d^{25} 1.711. Considerably higher thermal stability than UCl_5. Miscible with ethanol, ether, benzene, chloroform, pyridine, etc. Immediately decomposed in water.

REFERENCE:

R. G. Jones, E. Bindschadler, G. Karmas, F. A. Yoeman and H. Gilman. J. Amer. Chem. Soc. 78, 4287 (1956).

Uranium (VI) Ethoxide

$U(OC_2H_5)_6$

$$U(OC_2H_5)_5 + NaOC_2H_5 = NaU(OC_2H_5)_6$$

$$2\,NaU(OC_2H_5)_6 + (C_6H_5CO)_2O_2 = 2\,U(OC_2H_5)_6 + 2\,C_6H_5COONa$$

A 500-ml. three-neck flask is fitted with a gas-tight stirrer and a gas outlet tube. This flask is used to prepare a sodium ethoxide solution from 300 ml. of absolute alcohol and 1.69 g. (0.074 g.-atoms) of Na. When all of the Na is dissolved, the solution is cooled under N_2 and 20 ml. (34 g., 0.074 moles) of uranium (V) ethoxide (see above for preparation) is added with a pipette. The brown color of the ethoxide disappears, and a clear, light-green solution of $NaU(OC_2H_5)_6$ is formed. Now, 8.90 g. (0.037 moles) of dry benzoyl peroxide powder is added in three equal portions at about 10-minute intervals while vigorously stirring. The mixture becomes warm, acquiring a red color and forming a gelatinous precipitate of sodium benzoate. After one hour of additional stirring under N_2, half of the material is transferred (still under N_2) to a 250-ml. Claisen flask fitted with a distilling condenser, and the alcohol is distilled out at atmospheric pressure on a steam bath. The second half is then added and the procedure repeated.

The receiver flask is now heated on an oil bath and the contents are subjected to a vacuum distillation. At first, with the bath temperature as high as 140°C and at 5-10 mm., the last of the alcohol is removed; the uranium (VI) ethoxide distills out at the same bath temperature but at a high vacuum (0.003 mm.). Yield: 20 g. Rectification in high vacuum affords the pure product. Yield: 16 g. (43%). The boiling point is 72-74°C at 0.001 mm.

SYNONYM:

Uranium (VI) ethylate.

PROPERTIES:

Red, mobile liquid; d 1.563. Monomeric in benzene. Readily soluble in benzene, ether, petroleum ether, etc. Extremely sensitive to moisture; forms uranyl hydroxide when hydrolyzed. Strong oxidizing agent. Readily reduced to uranium (V) ethoxide. Synproportionates with U (IV) ethoxide according:

$$U(OC_2H_5)_6 + U(OC_2H_5)_4 = 2\,U(OC_2H_5)_5$$

REFERENCE:

R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, J. R. Thirtle, F. A. Yoeman and H. Gilman. J. Amer. Chem. Soc. 78, 6030 (1956).

Uranyldibenzoylmethane

$$UO_2(C_{15}H_{11}O_2)_2$$

$$\underset{(2\,H_2O)}{UO_2(CH_3COO)_2} + 2\,C_{15}H_{12}O_2 = UO_2(C_{15}H_{11}O_2)_2 + 2\,CH_3COOH$$

424.2 448.5 716.6

Methanolic solutions of uranyl acetate and dibenzoylmethane are combined in the cold. An intense reddish-yellow color appears at once, and after a few seconds uranyldibenzoylmethane powder begins to separate; it can be recrystallized from a large amount of hot alcohol. Other solvents may also be used for purification; however, one must bear in mind that uranyldibenzoylmethane forms well-crystallized addition compounds with almost all solvents.

Used analytically for the rapid separation of rare earths produced in the fission of uranium, since these do not form complexes with dibenzoylmethane in the presence of water. The uranium can be rapidly and conveniently separated by extraction (as the UO_2 complex).

PROPERTIES:

Orange-red crystals, which change color at about 180°C and begin to decompose at 245°C. Readily soluble in all ketones and esters and in pyridine; moderately soluble in ethyl alcohol; sparingly soluble in ether; insoluble in hydrocarbons such as benzene, toluene and naphtha. Stable to water, but is decomposed by acids and alkalies (even by ammonia).

REFERENCES:

H. Götte. Z. Naturforsch. 1, 378 (1946). Preparation of dibenzoylmethane: A. Magnani and S. M. McElvain. Org. Syntheses, collective Vol. 3, p. 251, New York-London, 1955.

SECTION 25

Manganese

H. LUX

Manganese

Mn

I. BY ELECTROLYSIS

Very pure Mn may be produced by electrolysis under the following conditions:

The electrolysis is performed with anode and cathode spaces separated from each other, using canvas or a ceramic substance as the cell diaphragm. The cathode electrolyte contains 70 g. of $MnSO_4 \cdot 4H_2O$ and 200 g. of $(NH_4)_2SO_4$ per liter, the anode electrolyte 100 g. of $(NH_4)_2SO_4$ per liter. The cathode is a polished stainless steel sheet; the anode is a lead sheet. The cathodic current density is 0.16 amp./in.^{2} and the temperature of the electrolyte should not exceed 40°C. The pH value in the cathode cell should be maintained between 4.5 and 8.5, and the free sulfuric acid content of the anode cell should not exceed 5%. To prevent oxidation of the catholyte and to promote uniform deposition of Mn, a small quantity of a saturated SO_2 solution is added from time to time to the catholyte so that a concentration of about 0.1–1 g. of SO_2/liter is maintained in it.

The current efficiency is about 50–70%. In addition to impurities, the content of which is a function of the purity of the starting electrolyte, the metal contains up to 0.02% S and some H_2; however, the latter can be readily removed by heating in vacuum. The γ-Mn product is silver-gray, polishes readily and is stable in air. The boundary layer in contact with the cathode shows gradual transition to fine-grained β-Mn and is therefore hard. If performed under different conditions, the electrolysis will produce shiny layers of metal which rapidly turn dark upon exposure to air; in this case the metal should be immersed in a 5% $Na_2Cr_2O_7$ solution immediately upon removal from the electrolyte; this treatment passivates it and permits it to retain its lustrous surface.

II. BY DISTILLATION

Very pure Mn can be obtained by the distillation of Mn prepared via the aluminothermic or the electrolytic methods. The metal, in a sintered Al_2O_3 boat, is placed in a ceramic tube closed at one end. The tube must be pretested for gas tightness, and a vacuum of at least 0.005 mm. Hg should be established in it. The tube is heated in a Globar furnace to a temperature of 1250 to 1350°C, at which temperature the Mn vapor pressure is 1-2 mm. The distilled metal deposits as small needles on a tubular nickel sleeve cooled by running cold water and located in the vicinity of the boat; the metal can be loosened by slight tapping. The product is extremely reactive and ignites upon exposure to air; all subsequent handling must therefore take place in an Ar atmosphere in the absence of O_2.

Manganese prepared under the same conditions but deposited on an uncooled surface, e.g., an alumina rod, is less reactive. The dense, silvery scales of the crystalline metal are easily stripped off and reduced to powder. This product is the α-modification, which is stable at temperatures below 742°C.

PROPERTIES:

Atomic weight 54.93. M.p. 1212°C, b.p. 2152°C. Electrolytically precipitated Mn: d 7.2, crystal structure γ-Mn, A6 type. Distilled Mn: d 7.44, crystal structure α-Mn, A12 type.

PrepBooks

REFERENCES:

I. R. Springer. Die elektrolytische Abscheidung des Mangans [The Electrolytic Deposition of Manganese], Akad. Verlagsges., Leipzig, 1951; S. M. Shelton and M. B. Royer. Trans. Electrochem. Soc. 74, 447 (1938), Chem. Zentr. 1939, I, 2284; I. A. Mendelev, S. I. Orlova and Y. S. Shpichinetskiy. Tsvet. Metal. 16, 53 (1941), Chem. Zentr. 1942, II, 2196; E. Herrmann. Ann. Physik [5] 21, 139 (1934).

II. R. Schenk and A. Kortengräber. Z. anorg. allg. Chem. 210, 273 (1933); H. Haraldsen and W. Klemm. Ibid. 220, 164 (1934); M. L. V. Gayler. Metallwirtschaft 9, 678 (1930); M. Picon and J. Flahaut. Comptes Rendus. Hebd. Séances Acad. Sci. 237, 569 (1953).

Manganese (II) Oxide

MnO

$$\underset{(\cdot 6\,H_2O)\ 287.0}{Mn(NO_3)_2} = MnO_2 + 2\,NO_2;\quad MnO_2 + H_2 = \underset{70.9}{MnO} + H_2O$$

The oxide varies from grassy green to light green and may be obtained from any of the oxides (or other suitable salts of

manganese) by reduction with H_2 at temperatures below 1200°C. Thus, for example, $Mn(NO_3)_2 \cdot 6H_2O$ is heated in air to about 300°C; the product (approx. $MnO_{1.95}$) is ground to powder and reduced for 4 hours at 800°C with pure, oxygen-free hydrogen; the reaction rate becomes appreciable about 450°C. With prolonged heating or high temperatures the product turns an increasingly grayish color and finally becomes light gray; in the presence of oxygen, it is brown. A reduction temperature of 800°C is sufficient for hydrated oxides; $MnCO_3$ must be heated to 1000–1100°C for 15–20 minutes.

PROPERTIES:

M. p. 1785°C; d 5.18. Crystal structure: B 1 (rock salt) type.

REFERENCES:

P. Dubois. Ann. Chimie [11] 5, 432; for preparation by heating $MnCO_3$ or MnC_2O_4 in a high vacuum, see M. LeBlanc and G. Wehner. Z. phys. Chem. A 168, 61 (1934); T. E. Moore, M. Ellis and P. W. Selwood. J. Amer. Chem. Soc. 72, 856 (1950); for preparation by heating $MnCO_3$ in flowing N_2, see H. Ulich and H. Siemonsen. Arch. Eisenhüttenwesen 14, 27 (1940); Z. Elektrochem. 45, 637 (1939).

Manganese (II) Hydroxide

$Mn(OH)_2$

$$\underset{(\cdot 4H_2O)\ 197.9}{MnCl_2} + 2\,KOH = \underset{112.2}{Mn(OH)_2} + \underset{89.0}{2\,KCl} \qquad \underset{149.1}{}$$

In the method of Simon, a solution of 300 g. of analytically pure KOH in 500 ml. of water in a round-bottom flask (see Fig. 327) is heated for about one half hour while a stream of completely O_2-free hydrogen is passed through; a completely O_2-free solution of 15–17 g. of $MnCl_2 \cdot 4H_2O$ in 15 ml. of boiled water is then added from a dropping funnel. The mixture is then heated to 190–200°C (as rapidly as possible) on an oil bath while H_2 is bubbled through. When the amorphous precipitate of $Mn(OH)_2$ is completely dissolved, the flask is allowed to cool slowly on the oil bath, whereby the compound precipitates out as white flakes of pearly sheen.

After cooling to room temperature, boiled water prepurged with H_2 is added from a dropping funnel until the flask is almost filled; the liquor is then siphoned off by means of a glass tube which

reaches almost to the bottom of the flask (the flow of H_2 should not be interrupted either during this or the preceding operation). The glass tube is connected to a Pyrex glass filter (constantly flushed with a H_2 stream), which in turn is attached to a suction flask; the latter is connected to the suction pump by way of a wash bottle containing a solution of $CrCl_2$. The addition of small amounts of water (washing operation) to the flask is repeated several times. The crystals are transferred (by shaking the flask) to the glass filter, washed on the filter, first with a large quantity of O_2-free water (a second dropping funnel is used), then with absolute alcohol through which H_2 is bubbled, and finally with peroxide-free ether. The product, still on the glass filter, is then dried in a desiccator over P_2O_5 while maintaining a high vacuum.

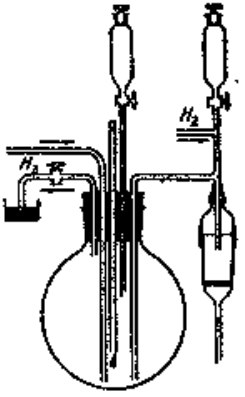

Fig. 327. Preparation of manganese(II) hydroxide.

This procedure gives a moderate yield of a well-crystallized product. Larger amounts of the microcrystalline substance are prepared more conveniently by the method of Scholder and Kolb [boiling with concentrated sodium hydroxide to which $(NH_3OH)Cl$ is added].

DropBooks

PROPERTIES:

When free of alkaline hydroxides and amorphous components, the dry product can be kept in an air-filled desiccator for weeks. The crystalline compound occurs in nature as pyrochroite.

Solubility (18°C) 0.0019 g./liter. d 3.258. Crystal structure; type C 6.

REFERENCES:

A. Simon, Z. anorg. allg. Chem. 232, 369 (1937); T. E. Moore, M. Ellis and P. W. Selwood, J. Amer. Chem. Soc. 72, 858 (1950); R. Scholder and A. Kolb, Z. anorg. allg. Chem. 264, 211 (1951).

Manganese (III) Oxide

γ-Mn_2O_3, γ-MnO(OH)

$$\underset{446.1}{2\,MnSO_4 \cdot 4\,H_2O} + \underset{34.0}{H_2O_2} + \underset{68.0}{4\,NH_3} = \underset{175.9}{2\,MnO(OH)} + \underset{264.3}{2\,(NH_4)_2SO_4} + 6\,H_2O$$

The method of Marti gives γ-MnO(OH) with a well-defined x-ray pattern. A solution of 2.2 g. of $MnSO_4 \cdot 4\,H_2O$ (10 mmoles)

in 350 ml. of water is treated in a large beaker (very vigorous mechanical agitation) with 34 ml. of a 3% H_2O_2 solution (30 mmoles). With continued very vigorous agitation, 50 ml. of a 0.2 M NH_3 solution (10 mmoles) is added at once from a graduated cylinder. The dark-brown or black suspension, which is evolving oxygen, is brought to a boil as rapidly as possible. The boiling is continued for about 4 minutes and the solution is filtered, washed with 1.5 liters of hot water, and dried over P_2O_5 in vacuum at temperatures below about 100°C.

Careful dehydration of γ-MnO(OH) (vacuum, 250°C) yields γ-Mn_2O_3. γ-MnO(OH) occurs in nature as manganite.

REFERENCES:

W. Marti. Uber die Oxidation von Manganhydroxyd und über höherwertige Oxyde und Oxydhydrate des Mangans [The Oxidation of Manganese Hydroxide and the Higher Oxides and Hydrated Oxides of Manganese], Thesis, Univ. of Bern, 1944, p. 83; W. Feitknecht and W. Marti. Helv. Chim. Acta 28, 142 (1945); T. E. Moore, M. Ellis and P. W. Selwood. J. Amer. Chem. Soc. 72, 861 (1950); P. Dubois. Ann. Chimie [11] 5, 434 (1936); A. Simon and S. Fehér. Z. Electrochem. 38, 137 (1932); F. Krull. Z. anorg. allg. Chem. 208, 134 (1932); K. L. Orr. J. Amer. Chem. Soc. 76, 857 (1954).

Manganese (IV) Oxide

MnO_2

$$\underset{287.0}{Mn(NO_3)_2 \cdot 6\,H_2O} = \underset{86.9}{MnO_2} + 2\,NO_2 + 6\,H_2O$$

The starting $Mn(NO_3)_2 \cdot 6\,H_2O$ is decomposed in air by heating to about 190°C; the product is ground to powder, boiled with nitric acid (conc. HNO_3 diluted 1:6) and heated in air to 450–500°C. The x-ray pattern of the product clearly shows the lines of pyrolusite (β-MnO_2). At atmospheric pressure, oxygen begins to split off above 530°C in air, and above 565°C in oxygen.

Alternate methods: a) From $MnCl_2$ and $(NH_4)_2S_2O_8$ in aqueous solution [A. Simon and F. Fehér, Z. Elektrochem. 38, 137 (1942)].

b) From NH_4MnO_4 and NH_3 in aqueous solution (A. Harzer, German Patent 713,904, Class 12, Group 3, as well as the references cited below).

c) From Mn_2O_7 [P. Dubois, Ann. Chimie [11] 5, 411 (1936); A. Simon and F. Fehér, Kolloid-Z. 54, 50 (1931); A. Simon and F. Fehér, Z. Elektrochem. 38, 137 (1932)].

SYNONYM:

Manganese dioxide.

REFERENCES:

C. Drücker and R. Hüttner. Z. phys. Chem. 131, 263 (1928); O. Glemser. Ber. dtsch. chem. Ges. 72, 1879 (1939); F. Krüll. Z. anorg. allg. Chem. 208, 134 (1932); W. Marti. Thesis, Univ. of Bern, 1944; T. E. Moore, M. Ellis and P. W. Selwood. J. Amer. Chem. Soc. 72, 863 (1950); G. Butler and H. R. Thirsk. J. Electrochem. Soc. 100, 297 (1953); G. Gattow and O. Glemser. Z. anorg. allg. Chem. 309, 121 (1961).

Manganese (VII) Oxide

Mn_2O_7

$$\underset{316.1}{2\,KMnO_4} + \underset{196.2}{2\,H_2SO_4} = \underset{272.3}{2\,KHSO_4} + \underset{221.9}{Mn_2O_7} + H_2O$$

Concentrated H_2SO_4 (15 ml., d 1.84) is placed in a dry porcellain mortar precleaned with chromosulfuric acid; then 23 g. of $KMnO_4$ is carefully added over a period of 10–15 minutes, while constantly stirring with a pestle. To obtain the desired result, the following precautions must be observed: only very pure $KMnO_4$ crystals, free of dust and organic substances (preferably Merck A.R. quality; do not reduce the crystals to powder), can be used. The reaction slurry should be left standing overnight in a dry spot, protected against dust. Porous pyrolusite is formed during this time, and the Mn_2O_7 oil is very gently kneaded out from it. Proper safety measures must be observed during the preparation and further workup of the material, since it often explodes for no apparent reason (an asbestos face shield with safety glasses and heavy leather gloves should be worn and one should work behind heavy glass plate and a fine wire screen).

Yield: 10 g. (62%). The product is entirely free of K^+ and SO_4^{2-}.

SYNONYMS:

Manganese heptoxide, permanganic acid anhydride.

PROPERTIES:

An oil with green metallic luster in reflected light; dark red in transmitted light; specific odor. M.p. 5.9°C; d_4^{20} 2.396; heat

of formation: −177.4 kcal (20°C); dissociation at approx. 55°C, detonation at 95°C. In vacuum, rapid and explosive dissociation above 10°C. Forms α-Mn_2O_3 during explosive decomposition, γ-MnO_2 during slow dissociation. Soluble in conc. H_2SO_4 and H_3PO_4 with an olive green color. Hygroscopic; dissociates slowly in humid air to MnO_2, liberating O_3-containing O_2 and, occasionally, a red mist of $HMnO_4$. Stable under refrigeration (−10°C) provided anhydrous conditions are maintained. Reacts explosively with most organic compounds; attacks acetic acid, acetic anhydride and CCl_4 even below room temperature. *Dangerous compound*! The impact sensitivity of Mn_2O_7 is equal to that of mercuric fulminate.

REFERENCES:

J. M. Lovén. Ber. dtsch. chem. Ges. 25, Ref. 620 (1892); A. Simon and F. Fehér. Z. Elektrochem. 38, 138 (1932); O. Glemser and H. Schröder. Z. anorg. allg. Chem. 271, 294 (1953).

Sodium Manganate (V)

$$Na_3MnO_4 \cdot 0.25\,NaOH \cdot 12\,H_2O$$

$$\underset{316.1}{2\,KMnO_4} + \underset{504.3}{2\,Na_2SO_3 \cdot 7\,H_2O} + \underset{240.0}{6\,NaOH} + \underset{72.1}{4\,H_2O}$$

$$= \underset{736.2}{2\,Na_3MnO_4 \cdot 10\,H_2O} + \underset{284.1}{2\,Na_2SO_4} + \underset{112.2}{2\,KOH}$$

A solution of 2 g. of very fine $KMnO_4$ powder in 50 ml. of 28% sodium hydroxide is triturated in a small Erlenmeyer flask with 3.5 g. of finely divided $Na_2SO_3 \cdot 7\,H_2O$; the flask stands in an ice bath. The trituration requires about 10 minutes, that is, until a light-blue crystalline slurry is obtained. This is then transported by vacuum onto an ice-cooled glass filter, and the product washed thoroughly with 28% sodium hydroxide at 0°C. The wet preparation is rapidly spread in a thin layer on fresh clay and stored at 0°C in an evacuated desiccator (no drying agent). The salt has the stoichiometric composition and contains, in addition to the hydroxide, about 0.4% SO_3; the preparative procedure should be designed to keep contamination by silicates or aluminates to a minimum.

PROPERTIES:

Formula weight 368.1. The salt, in the form of well-crystallized sky-blue rods, remains stable at 0°C if kept free of H_2O

and CO_2. Solubility in 28% NaOH at 0°C is equivalent to 0.06% Mn_2O_5. A solution of the salt in 50% potassium hydroxide turns grassy green upon heating or dilution; simultaneously, MnO_2 is precipitated according to the equation:

$$2\,Na_3MnO_4 + 2\,H_2O = Na_2MnO_4 + MnO_2 + 4\,NaOH.$$

REFERENCES:

H. Lux. Z. Naturforschg. 1, 281 (1946) and unpublished work. The preparation of the sulfate-free product is described by R. Scholder, D. Fischer and H. Waterstradt, Z. anorg. allg. Chem. 277, 236 (1954).

Potassium Manganate (VI)

K_2MnO_4

$$\underset{316.1}{2\,KMnO_4} + \underset{112.2}{2\,KOH} = \underset{394.2}{2\,K_2MnO_4} + {}^1/_2\,O_2 + H_2O$$

A solution of 30 g. of KOH in 50 ml. of water is prepared; 10 g. of $KMnO_4$ is added and the mixture is boiled in an open 250-ml. Erlenmeyer flask until a pure green solution is obtained. The water lost by evaporation is then replaced and the flask set in ice. The precipitated black-green crystals, which show a purplish luster, are collected on a Pyrex glass filter, washed (high suction) with some 1 N potassium hydroxide, and dried over P_2O_5. The salt can be recrystallized by dissolving in dil. potassium hydroxide and evaporating in vacuum.

PROPERTIES:

Formula weight 197.1. Solubility (20°C) in 2 N potassium hydroxide 224.7 g./liter, in 10 N potassium hydroxide 3.15 g./liter.

REFERENCES:

K. A. Jensen and W. Klemm. Z. anorg. allg. Chem. 237, 47 (1938); R. Luboldt. J. prakt. Chem. 77, 315 (1859). Preparation of an especially pure, KOH-free product is described by R. Scholder and H. Waterstradt, Z. anorg. allg. Chem. 277, 172 (1954).

Barium Manganate (VII)

$Ba(MnO_4)_2$

$$\underset{316.1}{2\,KMnO_4} + \underset{261.4}{Ba(NO_3)_2} + \underset{315.5}{Ba(OH)_2 \cdot 8\,H_2O} = \underset{512.6}{2\,BaMnO_4} + {}^1/_2\,O_2 + 2\,KNO_3 + 9\,H_2O$$

$$\underset{768.9}{3\,BaMnO_4} + \underset{44.81.}{2\,CO_2} = \underset{394.7}{2\,BaCO_3} + \underset{86.9}{MnO_2} + \underset{375.2}{Ba(MnO_4)_2}$$

A solution of 100 g. of $KMnO_4$ and 100 g. of $Ba(NO_3)_2$ in 1.5 liters of boiling water is prepared and treated with 20 g. of $Ba(OH)_2 \cdot 8\,H_2O$. The solution is heated on a water bath with frequent agitation until the evolution of O_2 largely ceases, whereupon another 20 g. of $Ba(OH)_2 \cdot 8\,H_2O$ is added and the water lost by evaporation replaced. The procedure is continued until the liquid becomes colorless. When the sparingly soluble $BaMnO_4$ settles out (together with some MnO_2 and $BaCO_3$), the liquid is decanted, the precipitate washed repeatedly with several liters of boiling water, boiled with a dilute solution of $Ba(OH)_2$, and rewashed thoroughly with boiling water.

The precipitate is then suspended in 1 liter of water and completely decomposed by introducing simultaneously CO_2 and superheated steam. This takes a few hours. The solution is left to settle; the liquor is suction-filtered through glass and concentrated until the almost black crystals appear upon cooling. The yield is 65–80 g. (80 to 100% of theory). Permanganates of all types of metals can be prepared by reacting the $Ba(MnO_4)_2$ with an equivalent quantity of sulfate.

SYNONYM:

Barium permanganate.

PROPERTIES:

Sparingly soluble in water; d 3.77.

REFERENCES:

W. Muthmann. Ber. dtsch. chem. Ges. 26, 1017 (1893); H. G. Grimm, C. Peters and H. Wolff. Z. anorg. allg. Chem. 236, 73 (1938).

Silver Manganate (VII)

$AgMnO_4$

$$\underset{158.0}{KMnO_4} + \underset{169.9}{AgNO_3} = \underset{326.8}{AgMnO_4} + \underset{101.1}{KNO_3}$$

A hot (80°C) solution of 5 g. of $AgNO_3$ in 100 ml. of water is added to a hot (80°C) solution of 4.66 g. of $KMnO_4$ in 300 ml. of water to which a drop of conc. nitric acid has been added. The mixture is permitted to cool. Since the product still contains some K, it is recrystallized from water by slow cooling from 80°C.

The black, lustrous, needle-shaped crystals tend to decompose on prolonged storage. Because of its limited solubility, this salt is less suitable as a raw material for other permanganates than $Ba(MnO_4)_2$.

SYNONYM:

Silver permanganate.

PROPERTIES:

Solubility (room temperature) 9 g./liter H_2O; d 4.49. Crystal structure: type $H0_3$.

DropBooks

REFERENCE:

W. Büssem and K. Herrmann. Z. Kristallogr. A 74, 459 (1930).

$BaSO_4$-$KMnO_4$ Solid Solution

The solid solution (mixed crystals), described and examined in detail by Grimm and Wagner, is prepared simply by mixing together solutions of $Ba(NO_3)_2$ and K_2SO_4, both containing a high percentage of $KMnO_4$. As an example, the following conditions were found to be suitable:

A solution of 1.31 g. (5 mmoles) of $Ba(NO_3)_2$ and 50 g. of $KMnO_4$ in 1 liter of water is prepared; similarly, 0.87 g. (5 mmoles) of K_2SO_4 and 50 g. of $KMnO_4$ are dissolved in 1 liter of water. Heating is required in both cases. The clear solutions—suction-filtered through glass, if necessary—are brought to 50°C, added together, and allowed to stand for a short time at 50°C. The crystals are then separated by suction filtration.

Washing the mixed crystals with acetone until the wash liquid turns a light rose results in a product with a $KMnO_4$ content of 25–30 mole %; treatment with water, however, readily decomposes

the crystals. A more stable solid solution, containing 6-8 mole % $KMnO_4$, is obtained by washing with water at 50°C, rinsing with a SO_2 solution, and repeating the washing. It is possible to boil the rose to purple powder with solutions of SO_2 or other reducing agents without a change in composition. The surface of the compound is decomposed on prolonged exposure to sunlight (with precipitation of manganese oxides).

REFERENCES:

H. G. Grimm and G. Wagner, Z. phys. Chem. 132, 135 (1928); see also A. Benrath and H. Schackmann, Z. anorg. allg. Chem. 218, 139 (1934).

Potassium Manganese (III) Chloride

K_2MnCl_5

$$\underset{158.0}{KMnO_4} + \underset{291.8}{8\,HCl} + \underset{74.6}{KCl} = \underset{310.4}{K_2MnCl_5} + \underset{141.8}{2\,Cl_2} + \underset{72.1}{4\,H_2O}$$

In the method of Weinland and Dinkelacker the compound is prepared as follows: 5 g. of $KMnO_4$ powder is added (constant shaking) to 50 ml. of approx. 40% HCl (d 1.19). The initial fine, brown precipitate is slowly dissolved on frequent shaking, while copious quantities of Cl_2 are being evolved. The solution is left standing for two hours, then decanted from any black K_2MnCl_6 that may have precipitated, and conc. aqueous KCl is added dropwise to the deep dark-red to brown solution (constant agitation) until the liquid becomes nearly colorless. The crystalline, brownish K_2MnCl_5 precipitate is filtered off by suction and dried over KOH.

REFERENCES:

R. F. Weinland and P. Dinkelacker, Z. anorg. allg. Chem. 60, 173 (1908). For the hydrate $K_2MnCl_5 \cdot H_2O$, see C. E. Rice, J. Chem. Soc. (London) 73, 260 (1898).

Potassium Hexachloromanganate (IV)

K_2MnCl_6

$$\underset{277.9}{Ca(MnO_4)_2} + \underset{583.5}{16\,HCl} + \underset{298.2}{4\,KCl} = \underset{691.7}{2\,K_2MnCl_6} + \underset{111.0}{CaCl_2} + 8\,H_2O + 3\,Cl_2$$

In the method of Weinland and Dinkelacker, 5.0 g. of $Ca(MnO_4)_2$ is added (constant agitation) to 50 ml. of 40% hydrochloric

acid cooled with an ice-salt mixture. A solution of 2 g. of KCl in 8 ml. of water is added simultaneously in drops. The almost black, crystalline precipitate is rapidly separated by suction filtration and dried for a short time on a clay plate over conc. H_2SO_4.

PROPERTIES:

Formula weight 345.9. Small, translucent, deep dark-red crystals; liberates Cl_2 continuously even in dry air.

REFERENCE:

R. F. Weinland and P. Dinkelacker. Z. anorg. allg. Chem. 60, 173 (1908).

Manganese (II) Sulfide

MnS

α-MnS, GREEN, CUBIC

DropBooks

This modification, which has been thoroughly studied by x-ray techniques, is obtained via the method of Classen.

A boiling solution of about 10 g. of $MnCl_2 \cdot 4H_2O$ in 500 ml. of water containing a small quantity of $K_2C_2O_4$ is reacted with an excess of a 50% NH_3 solution and saturated at its boiling point with H_2S. Upon further heating, the initial flesh-colored MnS precipitate is rapidly converted to the stable dark-green α-modification. To remove any coprecipitated sulfur, the sulfide is boiled three times with a dil. solution of freshly prepared, colorless $(NH_4)_2S$ and, after filtering, washed successively with H_2S-containing water, alcohol and ether. It is dried in an oil-pump vacuum at 120°C.

The dry preparation of α-MnS(alabandite) is described by H. Haraldsen and W. Klemm, Z. anorg. allg. Chem. 220, 271 (1936); for the synthesis of MnS_2 (hauerite), see W. Biltz and F. Wiechmann, ibid. 228, 271 (1936).

PROPERTIES:

Formula weight 86.99. M. p. 1610°C; d 3.99. Crystal structure: B1 (rock salt) type.

REFERENCES:

H. Schnaase. Z. phys. Chem. (B) 20, 89 (1933); F. Mehmed and H. Haraldsen. Z. anorg. allg. Chem. 235, 194 (1938); A. Classen. Z. analyt. Chem. 16, 319 (1877).

β-MnS, RED, CUBIC

In the method of Schnaase, the γ-modification is obtained by introducing H_2S into a cold solution of 50 g. of $Mn(CH_3COO)_2 \cdot 4H_2O$ in 300 ml. of water. After some time, most of the sulfide settles on the bottom as a reddish-brown precipitate, while another fraction adheres to the glass wall as a beautiful, minium-red scale. The precipitate is washed with H_2S-saturated water (the preferred washing method is decantation), filtered off with suction while H_2S is being passed over it, washed again with alcohol and ether, and dried in an oil-pump vacuum at 80°C.

Crystal structure: B3 (sphalerite) type.

REFERENCES:

H. Schnaase. Z. phys. Chem. (B) 20, 89 (1933); F. Mehmed and H. Haraldsen. Z. anorg. allg. Chem. 235, 194 (1938).

γ-MnS, RED, HEXAGONAL

Schnaase prepares the γ-modification by first dissolving 20 g. of analytically pure $MnCl_2 \cdot 4H_2O$ and some NH_4Cl in 500 ml. of boiled water through which a stream of O_2-free N_2 is being bubbled. Then H_2S is introduced at the boiling temperature and $Mn(OH)_2$ is precipitated out with a slight excess of concentrated NH_3 solution. The precipitate is initially white, gradually turns a light pink upon further contact with H_2S, and finally assumes the color of red meat, while the sulfide forming the surface layer is first orange yellow and later turns vermilion red. After settling, the precipitate is washed twice by decanting with H_2S-saturated water and boiled for two days in a 10% NH_3 solution while H_2S is bubbled through. Finally it is washed by decanting several times with H_2S-saturated water, filtered off in the absence of air while under a N_2 stream, washed with alcohol and ether, and dried in an oil-pump vacuum at 80°C. Any coprecipitated sulfur is removed by extraction with boiling CS_2 under nitrogen.

Crystal structure: B4 (wurtzite) type.

The conversion of the two dry, metastable red MnS modifications to the stable form starts at 200°C. The rate is appreciable, and is higher at 300°C. The red modifications also differ from the α-form in their magnetic behavior.

REFERENCES:

H. Schnaase. Z. phys. Chem. (B) 20, 89 (1933); F. Mehmed and H. Haraldsen. Z. anorg. allg. Chem. 235, 194 (1938).

Manganese (III) Sulfate

$Mn_2(SO_4)_3$

$$\underset{316.1}{2\,KMnO_4} + \underset{392.3}{4\,H_2SO_4} = \underset{398.0}{Mn_2(SO_4)_3} + \underset{174.3}{K_2SO_4} + \underset{72.1}{4\,H_2O} + 2\,O_2$$

In the method of Domange, the crystalline $Mn_2(SO_4)_3$ is prepared by introducing 20 g. of $KMnO_4$ powder into 100 ml. of H_2SO_4 (d 1.84) contained in a porcelain crucible (agitation); the mixture is carefully heated for 10 minutes at 60°C while stirring vigorously, whereby vapors of the explosive Mn_2O_7 are removed. The solution is then heated to 70°C (or at most to 75°C) with continued very vigorous agitation and accurate temperature control (thermometer). Vigorous evolution of O_2 takes place while the liquid turns brown and becomes clouded, with a tendency for a spontaneous rise in temperature, so that the danger of an explosion persists. After about 15 minutes, with most of the reaction completed, the danger of an explosion passes. The mixture is now slowly (10 minutes) brought to 140°C with continued stirring and is finally raised to 200°C (in 15 minutes). Following slow cooling, the solution is washed twice by decantation with H_2SO_4 (d 1.84) to remove the K_2SO_4. The product is collected on a glass filter and placed on a clay plate. The latter is placed for three to four days in a desiccator containing P_2O_5. The H_2SO_4 may be completely removed by heating the preparation, together with a receiver cooled to −80°C, for about three hours at 200°C and high vacuum; the salt itself does not begin to decompose until about 300°C.

PROPERTIES:

Extremely hygroscopic salt consisting of small, dark-green needles. Soluble in 75.25% wt. % or more H_2SO_4 without alteration; a brown salt of composition $Mn_2(SO_4)_3 \cdot H_2SO_4 \cdot 6\,H_2O$ crystallizes out from dilute (preferably 70%) sulfuric acid [A.R.J.P. Ubbelohde, J. Chem. Soc. (London) 1935, 1605]. Sulfuric acid in concentrations lower than 52% produces hydrolysis.

REFERENCE:

L. Domange, Bull. Soc. Chim. France [5] 4, 594 (1937).

Cesium Manganese (III) Sulfate

$CsMn(SO_4)_2 \cdot 12\,H_2O$

$$Cs_2SO_4 + 2\,Mn(CH_3COO)_3 \cdot 2\,H_2O + 3\,H_2SO_4 \rightleftharpoons 2\,CsMn(SO_4)_2 \cdot 12\,H_2O + 6\,CH_3COOH$$

(M.W.): 361.2 — 351.6 — 294 — 1192 — 360

In Christensen's method, 5.3 g. (0.01 mole) of $Mn(CH_3COO)_3 \cdot 2\,H_2O$ is dissolved in sulfuric acid (conc. H_2SO_4 diluted 1:3), starting at room temperature. Then, a solution of 3.6 g. (0.01 mole) of Cs_2SO_4 in 10 ml. of sulfuric acid of the same concentration is added; the solution is first cooled to −25°C in order to accelerate the precipitation and then left to stand for a long time at −5°C. The alum crystals are filtered off with suction and stored in a hermetically sealed bottle.

SYNONYM:

Cesium manganese alum.

PROPERTIES:

Coral-red crystalline powder. Melts at 40°C in the water of hydration; however, turns brownish black slightly above room temperature. The hydrated Mn_2O_3 is precipitated upon addition of water. The corresponding Rb alum melts at room temperature.

REFERENCES:

O. T. Christensen, Z. anorg. Chem. 27, 329 (1901); H. Bommer, Z. anorg. allg. Chem. 246, 281 (1941).

Manganese Nitride

Mn_4N

The nitride is prepared from very reactive sublimed manganese. The metal is heated in an apparatus which permits the continuous measurement of the amount of N_2 used in the reaction. A completely O_2-free nitrogen is used, under a pressure of ~100 mm. and a temperature of 690°C. The reaction is continued until a constant final pressure is obtained (12-24 hours).

The product corresponds quite exactly to the formula Mn_4N (6.0% N; ϵ-phase according to Hägg) and is strongly ferromagnetic. Below 400°C the homogeneous region of the phase extends from about 6.0 to 6.5% N.

REFERENCES:

U. Zwicker. Z. Metallkunde 42, 277 (1951); R. Schenk and A. Kortengräber. Z. anorg. allg. Chem. 210, 273 (1933); G. Hägg. Z. phys. Chem. B4, 346 (1929); L. F. Bates, R. E. Gibbs and D. V. Reddi Pantulu. Proc. Phys. Soc. 48, 665 (1936); see also H. Nowotny. Z. Elektrochem. 49, 245 (1943).

For Mn_4P, Mn_2P, etc., see W. Blitz and F. Wiechmann, Z. anorg. allg. Chem. 234, 117 (1937).

Manganese (III) Acetate

$Mn(CH_3COO)_3$, $Mn(CH_3COO)_3 \cdot 2\,H_2O$

$Mn(CH_3COO)_3 \cdot 2\,H_2O$

$$\underset{^1/_{10}:}{4\,Mn(CH_3COO)_2 \cdot 4\,H_2O} + \underset{98.0}{} + \underset{15.8}{KMnO_4} + \underset{48.0}{8\,CH_3COOH}$$

$$= \underset{134.0}{5\,Mn(CH_3COO)_3 \cdot 2\,H_2O} + \underset{9.8}{CH_3COOK} + \underset{18.0}{10\,H_2O}$$

In the method of Christensen, the salt is obtained in the following manner: 19.6 g. (80 mmoles) of $Mn(CH_3COO)_2 \cdot 2\,H_2O$ powder is added to 200 ml. of glacial acetic acid at the boiling temperature of the latter, and is stirred until completely dissolved. Then, $KMnO_4$ powder (3.1 g. = 20 mmoles) is gradually added and the mixture heated for a short time with constant agitation. After cooling, 3 ml. of water is added to the dark-brown solution; the mixture is allowed to stand overnight. If the quantity of precipitate is too small, another 3 ml. of water is added and the solution stirred. The formation of crystallization nuclei is promoted by frequent rubbing of the container walls with a glass rod. As a rule, copious crystallization occurs within about one hour. If necessary, the solution is allowed to stand for a few more days (frequent agitation) until the mother liquor is almost colorless. The salt is then filtered off with suction, washed with some glacial acetic acid and recrystallized. The last procedure consists in dissolving 30 g. of salt in 200 ml. of glacial acetic acid (heating), filtering off and working up further in the manner described above. Finally, the salt is dried over CaO.

PROPERTIES:

The cinnamon-brown crystals of a silky luster are immediately decomposed by cold water (hydration).

In activity the compound is likely to be a complex salt with three nuclei, of the following structure: $[Mn_3(CH_3COO)_6(H_2O)_2\cdot(CH_3COO)_3 \cdot 4\,H_2O$.

REFERENCES:

O. T. Christensen. Z. anorg. Chem. 27, 325 (1901); R. F. Weinland and G. Fischer. Z. anorg. allg. Chem. 120, 161 (1921).

$Mn(CH_3COO)_3$

$$\underset{\text{in:}}{2\,Mn(NO_3)_2\cdot 6\,H_2O} + \underset{153.0}{15\,(CH_3CO)_2O} = \underset{46.4}{2\,Mn(CH_3COO)_3} + 4\,NO_2 + {}^1/_2\,O_2 + \underset{144.1}{24\,CH_3COOH}$$

Chrétien and Varga obtain the salt from $Mn(NO_3)_2$ and acetic anhydride. A mixture of 20 g. of $Mn(NO_3)_2 \cdot 6\,H_2O$ and 80 g. of acetic anhydride is heated slightly (shaking) until the vigorous, strongly exothermic reaction evolving large amounts of gas is well under way. When the reaction is completed, the homogeneous, oily liquid is cooled; the anhydrous acetate precipitates out as a brown, crystalline powder. The latter is collected on a glass filter, washed first with acetic anhydride and then with some ether to remove the odor of acetic acid, and stored in a closed container (anhydrous conditions). The yield, based on manganese, is 85%.

REFERENCE:

A. Chrétien and G. Varga. Bull. Soc. Chim. France [5] 3, 2387 (1936).

Potassium Trioxalatomanganate (III)

$K_3[Mn(C_2O_4)_3]\cdot 3\,H_2O$

$$\underset{158.0}{KMnO_4} + \underset{630.3}{5\,H_2C_2O_4\cdot 2\,H_2O} + \underset{138.2}{K_2CO_3} = \underset{490.3}{K_3[Mn(C_2O_4)_3]\cdot 3\,H_2O} + 12\,H_2O + 5\,CO_2$$

Cartledge and Ericks prepare the ferric ion-free compound (which is very sensitive to light) from analytically pure $KMnO_4$ according to the equation presented above. A solution of 31.5 g. (0.25 moles) of $H_2C_2O_4 \cdot 2\,H_2O$ in 200 ml. of water is heated in

a 500-ml. beaker to 70–75°C; then, 6.32 g. (0.04 moles) of $KMnO_4$ powder is added little by little (constant agitation) and as soon as the solution turns colorless, 6.9 g. (0.05 moles) of K_2CO_3 is introduced in a similar manner. The mixture is cooled to 4–5°C (frequent stirring) and diluted with 150 ml. of 0–1°C water.

In all of the following operations light must be excluded as much as possible. The oxidation to Mn^{3+} is effected through the gradual addition of 1.58 g. (0.01 mole) of $KMnO_4$ powder; the solution is then stirred for about 10 minutes at 0 to 2°C. The intense cherry-red liquid is then suction-filtered through a glass filter precooled to 0°C, and is collected in a similarly cooled beaker. Next, the solution is reacted with half its volume of ice-cold alcohol and left to crystallize for two hours in an ice-salt mixture.

The precipitate is collected on a precooled glass filter, washed four times with 25 ml. of 50 vol. % alcohol, then with 95% alcohol, absolute alcohol and finally (three times) with ether; all of the wash liquids must be ice cold. After filtration with suction, the deep reddish-purple crystals are spread in a thin layer and exposed to air for a few hours; they are stored in brown bottles. The yield is ~50%.

PROPERTIES:

Very pure product can be stored for a long time at 20°C in the absence of air; stable for an almost unlimited time at −6°C. Readily soluble in water: concentrated solutions are deep reddish-brown; very dilute or acidified solutions are yellowish-brown. The color change is due to the shift of the instantly established equilibrium:

$$[Mn(C_2O_4)_3]^{-3} + 2\,H_2O \rightarrow [Mn(C_2O_4)_2(H_2O)_2]^{-1} + C_2O_4^{-2}$$

The salt is a normal complex.

REFERENCE:

G. H. Cartledge and W. P. Ericks. J. Amer. Chem. Soc. 58, 2061 (1936).

Potassium Dioxalatodihydroxomanganate (IV)

$$K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2\,H_2O$$

$$\underset{158.0}{KMnO_4} + \underset{378.2}{3\,H_2C_2O_4\cdot 2\,H_2O} + \underset{92.1}{{}^1/_2\,K_2C_2O_4\cdot H_2O} = \underset{379.2}{K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2\,H_2O} + 3\,CO_2 + 6{}^1/_2\,H_2O$$

This compound, discovered by Cartledge and Ericks, is prepared in a manner quite similar to that of $K_3[Mn(C_2O_4)_3]$. Thus,

17.64 g. (0.14 moles) of $H_2C_2O_4 \cdot 2\,H_2O$ is dissolved in 250 ml. of water and the solution is cooled to 0°C; then, 6.32 g. (0.04 moles) of $KMnO_4$ powder and 4.78 g. (0.026 moles) of $K_2C_2O_4 \cdot H_2O$ are added with constant agitation. The mixture is stirred vigorously for about 20 minutes; the temperature should rise gradually to 7°C during this time. As soon as CO_2 begins to evolve at this temperature, the dark-green solution is rapidly cooled to 0°C in an efficient cooling mixture (swirling necessary) and is quickly suction-filtered through a Büchner funnel (filter paper). The filtrate is immediately placed in a cooling mixture and reacted with 100 ml. of alcohol in small portions at 0°C; the complex salt is thus precipitated as a very fine, crystalline powder. The latter is rapidly filtered off, washed successively with ice-cold 50% alcohol, 95% alcohol, absolute alcohol and ether, and stored at 0°C.

The salt can be recrystallized at 0°C: the powder is dissolved in 25 times its volume of cold 0.1 M oxalic acid, filtered rapidly at 0°C, the solution diluted with 1/6 its volume of ice-cold 95% alcohol and placed in a cooling mixture for crystallization. It is best to prepare the salt in a cold room, otherwise proper cooling becomes cumbersome.

PROPERTIES:

Green, crystalline salt; not homogeneous; consists of green and orange rods (probably the *cis* and *trans* forms). Rapidly decomposed at room temperature, particularly when exposed to light; remains stable for a few weeks at −6°C if light is excluded. Solutions are initially green, but rapidly turn brown and become clouded; solutions containing some oxalic acid kept at 0°C remain clear for some time.

REFERENCE:

G. H. Cartledge and W. P. Ericks, J. Amer. Chem. Soc. 58, 2061 (1936).

Potassium Hexacyanomanganate (I)

$K_5Mn(CN)_6$

$$\underset{\text{Wt.:}\ 90.9}{3\,Na_4Mn(CN)_6} + \underset{2.7}{Al} + \underset{16.0}{4\,NaOH} = \underset{97.8}{3\,Na_5Mn(CN)_6} + NaAl(OH)_4$$

$$\underset{97.8}{3\,Na_5Mn(CN)_6} + 15\,K^+ = \underset{121.9}{3\,K_5Mn(CN)_6} + 15\,Na^+$$

According to Manchot and Gall, the salt is best prepared by starting with $Na_4Mn(CN)_6 \cdot xH_2O$ (see p. 1473). Thus, 10 g. of the

salt is dissolved in 150 ml. of 2% sodium hydroxide (Erlenmeyer flask), the air being kept out during this operation by a stream of H_2. Then, 8 g. of Al granules is added little by little, but rather rapidly (2 minutes); the sparingly soluble $Na_2Mn[Mn(CN)_6]$ should not precipitate in the process. After about five minutes the solution becomes intensely yellow-brown; it is then rapidly suction-filtered through a Pyrex filter of small pore size. The filtrate is allowed to flow into 150 ml. of a solution containing 15 g. of KOH and 30 g. of KCN and saturated with KCl. The desired compound is thereby precipitated as a white, crystalline powder, only sparingly soluble in water; any Mn^{++} present remains in solution. The salt is separated by rapid filtration through a Pyrex filter and thoroughly washed, first with 200 ml. of 10% potassium hydroxide, then with 100 ml. of 20% KCN solution, and finally with about 700 ml. of boiled, ice-cold water (until the filtrate is completely colorless).

PROPERTIES:

The potassium salt obtained in the above manner is slowly oxidized in moist air, turning brown. The sodium salt solution is rapidly discolored in air; H_2 is liberated on boiling but there is a slow evolution even at room temperature.

DropBooks

REFERENCES:

W. Manchot and H. Gall, Ber. dtsch. chem. Ges. 61, 1135 (1928). Preparation by means of a sodium amalgam is described by W. D. Treadwell and W. E. Raths, Helv. Chim. Acta 35, 2277 (1952).

Potassium Hexacyanomanganate (II)

$$K_4Mn(CN)_6 \cdot 3\,H_2O$$

$$\underset{114.9}{MnCO_3} + \underset{390.6}{6\,KCN} + \underset{54.1}{3\,H_2O} = \underset{421.4}{K_4Mn(CN)_6 \cdot 3\,H_2O} + \underset{138.2}{K_2CO_3}$$

A paste of 20 g. of freshly precipitated $MnCO_3$ (see the next preparation) is placed in a flask from which the air has been displaced with N_2 and heated on a water bath to 70–80°C. A solution of 80 g. of KCN in 100 ml. of water is added slowly in drops and the mixture is maintained at this temperature for an additional half hour (occasional swirling). The small residue of undissolved $MnCO_3$ is removed by rapid filtration of the hot solution, air being excluded as completely as possible. The bluish-purple crystals which precipitate from the yellow solution on cooling are separated by suction filtration, washed with alcohol, and dried in a N_2 stream at room temperature.

Alternate method: Readily prepared from $Mn(CH_3CO)_2$ and KCN. The sodium compound $Na_4Mn(CN)_6$ is prepared in a completely similar manner; it is more soluble than the potassium salt.

SYNONYM:

Potassium manganese (II) cyanide.

PROPERTIES:

Soluble without being altered only in solutions which have a KCN concentration higher than 1.5 N; at lesser CN concentrations, the greenish $K_2Mn[Mn(CN)_6]$ is precipitated. The crystals effloresce in air with partial oxidation.

REFERENCES:

G. Grube and W. Brause. Ber. dtsch. Chem. Ges. 60, 2273 (1927); J. Meyer. Z. anorg. allg. Chem. 81, 390 (1913); P. Straus. Z. anorg. Chem. 9, 6 (1895).

Potassium Hexacyanomanganate (III)

$K_3Mn(CN)_6$

$$\underset{189.0}{MnSO_4 \cdot H_2O} + 2\,\underset{168.0}{NaHCO_3} = \underset{114.9}{MnCO_3} + Na_2SO_4 + CO_2 + 2\,H_2O$$

$$\underset{229.8}{2\,MnCO_3} + \underset{781.2}{12\,KCN} + \underset{34.02}{H_2O_2} = \underset{656.5}{2\,K_3Mn(CN)_6} + \underset{276.4}{2\,K_2CO_3} + \underset{112.2}{2\,KOH}$$

A fresh precipitate of $MnCO_3$ is prepared by slowly adding a solution of 50 g. of $MnSO_4 \cdot H_2O$ in 120 ml. water to a solution of 75 g. of $NaHCO_3$ in 950 ml. of water (20°C, good stirring; caution: the mixture tends to foam). The product is filtered off with suction, washed with a large amount of water, and, while still wet, thoroughly mixed with a solution of 135 g. of KCN in 270 ml. of water, producing a dark-blue solution of $K_4Mn(CN)_6$. Following cooling to ~15°C, 150 ml. of 3% H_2O_2 is added slowly and with stirring. The solution is allowed to stand for a few minutes until its color turns deep dark brown. With sufficient cooling no appreciable amount of O_2 is evolved.

The solution is now passed without delay through a suction filter (to remove any small residues of MnO_2 and similar compounds) and allowed to crystallize overnight in a refrigerator. The precipitated crystals (60–70 g., 63–74% yield based on $MnSO_4$)

are filtered off with suction, washed with alcohol and dried in a desiccator. An additional crop can be recovered from the mother liquor by covering it carefully with a layer (roughly the same volume) of alcohol and allowing to stand for several days.

If it is necessary to recrystallize the salt, it is covered with 8-10 times its volume of 10% KCN, rapidly heated on a water bath to 45°C (stirring), immediately suction-filtered, cooled with ice and covered with alcohol as described above.

SYNONYM:

Potassium manganese (III) cyanide.

PROPERTIES:

Dark red-brown needles; stable in air; decomposed by water, forming hydrated Mn_2O_3.

REFERENCES:

This procedure was developed in (unpublished) experiments in cooperation with E. Brodkorb; G. Grube and W. Brause. Ber. dtsch. chem. Ges. 60, 2273 (1927); J. Meyer. Z. anorg. allg. Chem. 81, 390 (1913).

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SECTION 26

Rhenium

O. GLEMSER

Rhenium Metal

Prepared by reduction of NH_4ReO_4 or $KReO_4$ with H_2.

I. Fine NH_4ReO_4 powder is slowly heated to 200–250°C in very pure H_2 and held at that temperature for three hours. The temperature is then raised to 500°C and the reduction completed at 1050°C (six hours). The boats and reactor tubes should be porcelain.

If heating rates are too high, part of the product evaporates as the oxide and deposits to form a mirror on the cooler parts of the tube.

II. $KReO_4$, in a silver boat, is reduced in very pure H_2 at 500°C. The product is extracted with H_2O containing a small amount of HCl, dried and again reduced with H_2 in a porcelain boat at 1000°C.

PROPERTIES:

Atomic weight 186.22. Gray metal powder; the solid has a platinum-like luster. M.p. 3170°C; d 20.35; Brinell hardness 250. Readily soluble in nitric acid and slowly in sulfuric acid. Crystal structure: A 3 type.

REFERENCES:

I. W. Biltz and G. A. Lehrer. Nachr. Gött. Ges. 1931, 193.
II. W. Biltz. Z. Elektrochem. 37, 498 (1931); W. Geilmann. Private communication.

Rhenium (III) Chloride

$ReCl_3$

$$Re + {}^3/_2\ Cl_2 = ReCl_3$$
$$186.2 \quad 33.0\,l. \quad 292.6$$

Rhenium metal is placed in a reactor consisting of a hard glass tube joined to a receiver manifold with seven bulbs

sealed on. The air is displaced with oxygen-free H_2 and the Re then heated in a stream of Cl_2. The raw sublimate is collected in the first bulb; it is resublimed into the second bulb under oxygen-free, dry N_2 (the less volatile $ReCl_3$ remains in the first bulb). The operation is repeated using the next set of bulbs, etc. The $ReCl_5$ fractions are then collected from all the bulbs and resublimed at 2-3 mm. and 500-550°C.

ANALYSIS:

Oxidation to ReO_4^- with sodium hydroxide + H_2O_2; the ReO_4^- ion is precipitated as nitron hydrogen perrhenate.

PROPERTIES:

Dark purple-red crystals. Bimolecular under normal conditions (Re_2Cl_6). Converted in moist air to $ReCl \cdot 2H_2O$ (2-3 hours); the water of hydration is readily removed by heating to 100°C in vacuum over P_2O_5. Soluble in water with a deep dark-red color; the solution turns cloudy after several hours because of hydrolysis, and black $Re_2O_3 \cdot H_2O$ is precipitated. Complete hydrolysis on boiling. Soluble in glacial acetic acid and dioxane (reddish-purple color), alcohol and liquid ammonia; slightly soluble in ether. A $AgNO_3$ solution produces a precipitate only after lengthy heating with nitric acid. Forms well-crystallized compounds with RbCl, CsCl and organic bases. Hexagonal crystal structure.

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REFERENCES:

W. Geilmann, F. W. Wrigge and W. Biltz. Nachr. Gött. Ges. 1932, 582; W. Geilmann and F. W. Wrigge. Z. anorg. alig. Chem. 214, 249 (1933); O. W. Kolling. Trans. Kansas Acad. Sci. 56, 378 (1953).

Rhenium (V) Chloride

$ReCl_5$

$$\underset{186.2}{Re} + \underset{55.0\,l.}{\tfrac{5}{2}\,Cl_2} = \underset{363.5}{ReCl_5}$$

Rhenium metal is placed in a boat which is inserted into the hard glass apparatus of Fig. 328. The air is displaced by O_2-free nitrogen and the Re chlorinated at 500°C in a stream of Cl_2. The evolving black-brown vapors are condensed at a as a black solid. The apparatus is sealed off at 1, connected at 5 to a high vacuum,

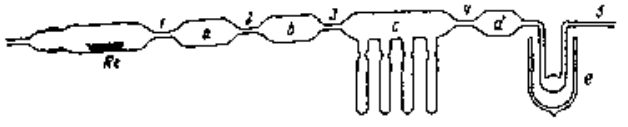

Fig. 328. Preparation of rhenium (V) chloride

evacuated and heated from 20 to 50°C; small fractions of the very volatile $ReOCl_4$ (b.p. 223°C) are then condensed in *d* and *e*. The bulk of the $ReCl_5$ is driven into *b* at 150 to 250°C, the tube melt-sealed at 2, and the substance sublimed at 200°C from *b* to *c*, leaving only a slight residue in *b*. Finally, the tube is melt-sealed at 3 and 4 and the preparation distributed (by shaking) into the small tubes attached at *c*; the latter are then melt-sealed.

PROPERTIES:

A deep, black-brown powder; dark brown vapor. Sensitive to air, sublimation at atmospheric pressure results in decomposition. Hydrolyzed by water, forming various products. Soluble in hydrochloric acid (green solution) with liberation of Cl_2.

REFERENCES:

W. Geilmann, F. W. Wrigge and W. Blitz, Angew. Chem. 46, 223 (1933); Z. anorg. allg. Chem. 212, 244 (1933).

Potassium Rhenium (IV) Chloride

K_2ReCl_6

$$\underset{186.2}{Re} + \underset{44.0\,l.}{2\,Cl_2} + \underset{149.1}{2\,KCl} = \underset{477.1}{K_2ReCl_6}$$

Fine Re powder is intimately ground with KCl (10% excess) and slowly heated to about 300°C in a porcelain boat, first under N_2 and then in a slow Cl_2 stream. The K_2ReCl_6 is formed immediately and only a slight quantity of rhenium chlorides is volatilized. Following cooling in a stream of N_2, the substance is dissolved in some hot 5% HCl and recrystallized; the remainder is obtained by concentration and crystallization during cooling.

Alternate method: Reaction of $KReO_4$ with KI and hydrochloric acid. The procedure is involved and it is difficult to obtain a pure product [H. Schmidt, Z. anorg. allg. Chem. 212, 188 (1933); O. W. Kolling, Trans. Kansas Acad. Sci. 56, 379 (1953)].

PROPERTIES:

Yellowish-green powder or regular green crystals. Melts with decomposition. Addition of conc. H_2SO_4 at moderate temperatures produces HCl. Fair solubility in water. Solubility in 12% HCl: 21.4 (0°C); 30.3 (18°C) g./liter; in 37% HCl: 3.3 (0°C); 3.7 (18°C) g./liter. d_4^{15} 3.34. Crystal structure: type $J1_1$.

REFERENCE:

W. Geilmann. Private communication.

Rhenium (VI) Oxychloride

$ReOCl_4$

Prepared via reaction of Re_2O_7 with $ReCl_5$.

Rhenium metal is chlorinated at 500°C in a stream of Cl_2 in the apparatus described for the preparation of ReO_3Cl. Following cooling, the Cl_2 is displaced with O_2 and the sections of the tube in which brown-black crystals of $ReCl_5$ have appeared are heated with a small flame to 50–70°C. The $ReCl_5$ melts (often with appearance of a flame) and the crystals turn into a brown liquid, which is then distilled in a stream of N_2 into a well-cooled U tube receiver. The excess Cl_2 is evaporated, the apparatus filled with O_2, and the liquid brought to a gentle boil. Heating at 200°C in an N_2 stream is continued for an hour in order to completely remove all traces of ReO_3Cl. Then about one third of the remaining liquid is distilled off. The receiver is now replaced by a fresh one and, except for a small residue, the remaining liquid is distilled over.

Alternate method: From $ReCl_5$ and dry O_2 at 110 to 130°C [O. W. Kolling, Trans. Kansas Acad. Sci. 56, 378 (1953)].

PROPERTIES:

Formula weight 344.05. Fibrous needles; dark orange in thin, brownish-red in thick layers. M.p. 29.3°C, b.p. 223°C (slight decomposition). Decomposes at 300°C. Immediately forms ReO_3Cl on heating in a stream of O_2. Hydrolyzed by water to rhenium (IV) hydroxide and $HReO_4$.

REFERENCE:

A. Brukl and K. Ziegler. Ber. dtsch. chem. Ges. 65, 916 (1932).

Rhenium (VII) Oxychloride

ReO_3Cl

Prepared by reaction of Re_2O_7 (excess) with $ReCl_5$.

Two boats, one containing five and the other two parts of Re, are placed in a high-melting glass reactor tube in a manner such that heating of one will not raise the temperature of the other. A U-shaped tube and two condensation traps are connected to the reactor by means of ground-glass joints (the traps are cooled to −65°C with alcohol-Dry Ice). The air in the apparatus is displaced with O_2 and the first boat (the one containing five parts of Re) is heated in a slow stream of O_2 in such a way that the Re_2O_7 formed is deposited in the tube (the U tube must be cooled to a low temperature during this operation). The oxygen is then displaced with Cl_2 and the second boat heated in a stream of Cl_2. The rhenium chlorides formed in this manner react with the Re_2O_7 and the products of this reaction are condensed in the U tube. Any cocondensed Cl_2 is evaporated; then, the ReO_3Cl is distilled over as the first fraction boiling above 100°C (it is usually very light blue or green). On repeated fractionation in a stream of N_2 the product becomes colorless.

Alternate method: From ReO_3 and dry Cl_2 at 160-190°C. Yields exceed 70% [C. J. Wolf, A. F. Clifford and W. H. Johnston, J. Amer. Chem. Soc. 79, 4257 (1957)].

PROPERTIES:

Formula weight 269.68. Colorless liquid; strongly light refracting. M.p. 4.5°C, b.p. 131°C (corr.). Reacts instantaneously with Hg, Ag, stopcock grease and numerous other organic compounds. Soluble in CCl_4. Hydrolyzes to $HReO_4$ and HCl.

REFERENCE:

A. Brukl and K. Ziegler, Ber. dtsch. chem. Ges. 65, 916 (1932).

Rhenium (IV) Oxide

ReO_2

1.

$$2\,Re_2O_7 + 3\,Re = 7\,ReO_2$$

$^1/_{14}$: 96.9 55.9 152.8

A stoichiometric mixture of Re and Re_2O_7 is heated to 300°C for one day in a small, evacuated, thick-wall quartz tube, which is

sealed by melting; the reactants are then heated to 600–650°C for an additional day. The product is orthorhombic ReO_2.

II. Heating of NH_4ReO_4 in vacuum at 500°C yields monoclinic ReO_2 of the MoO_2 type; above 500°C, orthorhombic oxides are formed.

PROPERTIES:

Formula weight 218.22. Gray-black powder; dissociates in a high vacuum at 1000°C to Re and Re_2O_7. Readily oxidized by O_2. Insoluble in weak acids, but dissolved by conc. halogen acids. Converted to $HReO_4$ by H_2O_2 and HNO_3. d_4^{25} 11.4. Heat of formation: —70 kcal.

REFERENCES:

I. W. Biltz, Z. anorg. allg. Chem. 214, 227 (1933).
II. W. H. Zachariasen, Amer. Crystallographic Assoc. Program and Abstracts of Winter Meeting, F 4 (1951); A. Magnéli, Acta Crystallogr. (Copenhagen) 9, 1038 (1956).

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Rhenium (VI) Oxide

ReO_3

I. REDUCTION OF Re_2O_7 BY CARBON MONOXIDE

$$\underset{484.4}{Re_2O_7} + \underset{22.4\ l.}{CO} = 2\,\underset{468.4}{ReO_3} + \underset{22.4\ l.}{CO_2}$$

The apparatus is a glass tube sealed at one end; about 1 g. of Re_2O_7 is sublimed into it in a stream of O_2. When the reaction is completed, the apparatus is evacuated and filled with CO to a pressure of 760 mm. The glass tube is then slowly heated to 175°C in a glycerol bath and held at that temperature until the preparation turns blue. The temperature is then slowly raised to 225°C and later, when red ReO_3 is formed, to 280°C. The run requires two to three hours. The yield is quantitative.

II. Reaction of Re_2O_7 with dioxane to form a complex compound, which dissociates at 125–145°C to ReO_3 and some volatile products.

The apparatus consists of a reaction flask protected against moisture; 4 ml. of dioxane is rapidly added to 1 g. of Re_2O_7 under anhydrous conditions (the dioxane should be predistilled

over Na metal). The mixture is gently heated on a water bath until a clear, colorless solution is obtained. Local overheating must be avoided, since it produces cloudy solutions and, ultimately, contaminated products. The flask is then placed in an ice bath to freeze the solution. After the freezing, the frozen substance is allowed to melt. The Re_2O_7-dioxane complex crystallizes in the form of a dense, pearly-gray precipitate; the excess dioxane becomes liquid. The freezing-melting operation is then repeated, the excess of dioxane decanted, and the compound dried in a vacuum desiccator at room temperature over conc. H_2SO_4. The dry complex is rapidly placed in a crucible and carefully heated on a hot plate (125 to 145°C). The substance is melted, forming a colorless to bluish-green liquid, which later dissociates to red ReO_3 and some volatile, Re-free products. The ReO_3 thus formed is pure. The yield is about 96%.

PROPERTIES:

Formula weight 234.22. Red powder. During reduction of Re_2O_7, the preparation passes through intermediate stages with hues ranging from green to dark blue (rhenium blue) until the final red color is obtained. Decomposed in high vacuum at 400°C to Re_2O_7 and ReO_3. Not attacked by hot hydrochloric acid, but converted to $HReO_4$ by strong HNO_3. Disproportionates in warm NaOH to ReO_3 and $NaReO_4$; $NaOH + H_2O_2$ instantaneously produce $NaReO_4$. d_4^{25} 6.9; heat of formation: −146.0 kcal. Crystal structure: $D0_9$ type.

REFERENCES:

I. A. D. Melaven, J. N. Fowle, W. Brickel and C. F. Hiskey in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York-Toronto-London, 1950, p. 187.
II. H. Nechamkin and C. F. Hiskey. Ibid., p. 186; H. Nechamkin, A. N. Kurtz, and C. F. Hiskey. J. Amer. Chem. Soc. 73, 2828 (1951).

Rhenium (VII) Oxide

Re_2O_7

$$\underset{372.4}{2\,Re} + \underset{78.41.}{^7/_2\,O_2} = \underset{484.4}{Re_2O_7}$$

The compound is prepared in a combustion tube to which a U tube is sealed on; the latter is attached to a condensation trap

Both ends of the tube are protected against humidity by vessels containing $CaCl_2$ and conc. H_2SO_4. The rhenium metal is placed in a porcelain boat situated in the front section of the tube, which is heated to 150°C while a very fast stream of oxygen is passed over the metal. Crystals of Re_2O_7 deposit in the front section of the tube and in the condenser tube (there is virtually no vapor mist); if the starting Re is not entirely alkali-free, some $KReO_4$ will remain in the boat. The Re_2O_7 should be resublimed in a stream of O_2.

The compound is used in the preparation of $HReO_4$, of the lower oxides and of very pure Re (reduction with H_2).

PROPERTIES:

Bright-yellow crystalline powder. M.p. 301.5°C, b.p. 362.4°C; d_4^{25} 6.103; heat of formation: −295.9 kcal. Extremely hygroscopic. Readily soluble in H_2O, forming $HReO_4$; soluble in alcohol; sparingly soluble in ether. Stored in melt-sealed glass tubes. Rhombic crystals.

REFERENCES:

W. Geilmann. Private communication; W. A. Roth and C. Becker. Z. phys. Chem. 159, 29 (1932); K. Wilhelmi. Acta Chem. Scand. 8, 693 (1954).

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Sodium Rhenate (IV)

Na_2ReO_3

$$\underset{218.2}{ReO_2} + 2\,\underset{80.0}{NaOH} = \underset{280.2}{Na_2ReO_3} + H_2O$$

The apparatus is shown in Fig. 329. A gold crucible *c* is introduced into the quartz apparatus through opening *e* and placed in

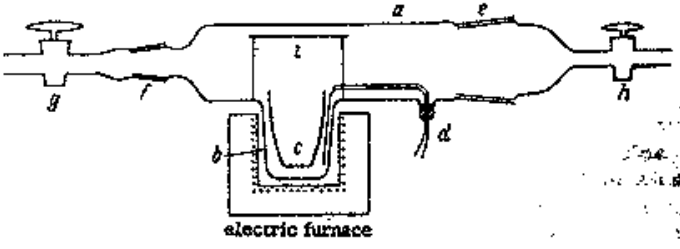

Fig. 329. Preparation of sodium rhenate (IV). *a* quartz tube; *b* crucible-shaped attachment; *c* gold crucible; *d* thermocouple; *e* movable gold shield (splash shield)

the attachment *b*; a stream of oxygen-free N_2 is passed from *h* to *g*. After thorough flushing with N_2, 10 g. of very pure and dry NaOH is introduced (through *f*) into *c*. The apparatus is then heated to 500°C and 4 g. of dry ReO_3 added by shaking to the melt. The ReO_3 dissolves, the melt turns reddish-brown, and water vapor escapes through *f*. After the reaction is completed, the heater is removed and attachment *b* cooled with ice water; this spalls the solidified melt off the crucible walls. The fused material contains (clearly separated) an upper layer of NaOH and a lower stratum of the brown rhenate. The fused cake is gently crushed, leached with deaerated ice water, decanted, filtered in the absence of air, washed with alcohol and dried, again in the absence of air. The filtering and drying device shown in Fig. 52, p. 74, is handy in this operation.

Alternate method: Fusion of ReO_3 with NaOH [W. Geilmann, F. W. Wrigge and W. Biltz, Z. anorg. allg. Chem. 214, 233 (1933)].

SYNONYM:

Sodium rhenite.

PROPERTIES:

Brown powder. On heating in air, converts to the yellow perrhenate. Insoluble in H_2O and in bases; soluble in conc. hydrochloric acid, converting to the green H_2ReCl_6.

REFERENCE:

I. and W. Noddack. Z. anorg. allg. Chem. 215, 134 (1933).

Ammonium Perrhenate

NH_4ReO_4

$$\underset{484.4}{Re_2O_7} + 2\,NH_3 + H_2O = \underset{536.6}{2\,NH_4ReO_4}$$

A solution of Re_2O_7 in some water is prepared, excess ammonia is added and the solution evaporated in a platinum crucible placed on a water bath.

Alternate method: Rhenium sulfides, oxides or rhenium metal are dissolved in HNO_3. The solution is evaporated and diluted with ammonia. Recrystallization is required! May be used to prepare pure rhenium (see p. 1476).

PROPERTIES:

Thick, white, hexagonal crystals. Dissociates in air above 200°C to form NH_3, H_2O and Re_2O_7. Solubility: 2.9 (0°C); 6.2 (20°C); 32 (80°C) g. of salt/100 g. H_2O; d 3.63. Crystal structure: HO_4 type.

REFERENCE:

I. and W. Noddack. Z. anorg. allg. Chem. 181, 23 (1929).

Barium Perrhenate

$Ba(ReO_4)_2$

An aqueous solution of Re_2O_7 (= $HReO_4$) is neutralized exactly with baryta water, using neutral red as the indicator. The residue is dried, and the water-containing salt is converted to anhydrous $Ba(ReO_4)_2$ in vacuum or by heating to 120°C.

PROPERTIES:

Formula weight 637.80. Colorless columns or rhomboids. Solubility: 1.8 (0°C); 5.3 (20°C); 47 (70°C) g. of salt/100 g. H_2O. Solubility in alcohol: 2.4 g/liter of solution at 18.5°C.

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REFERENCES:

I. and W. Noddack. Z. anorg. allg. Chem. 181, 25 (1929); W. Lewino. Thesis, Univ. of Hamburg, 1932.

Barium Rhenate (VI)

$BaReO_4$

Prepared by reducing $Ba(ReO_4)_2$ with ReO_2 and NaOH in a melt. The apparatus is the same as that used in the preparation of Na_2ReO_3 (Fig. 329). Sodium hydroxide (20 g.) is fused in crucible *c* under a stream of N_2; then, 8.00 g. of $Ba(ReO_4)_2$ is added, followed by 2.00 g. of ReO_2. The melt is heated to 500°C and held at that temperature for one hour. It is then cooled to 300°C and held at that temperature for one hour. The heater is then removed and attachment *b* cooled with ice water. The melt cake is broken up and treated with 96% alcohol at 0°C; this loosens the NaOH and $NaReO_4$ in the melt: the former reacts with any unconverted $Ba(ReO_4)_2$ to form $NaReO_4$ and $Ba(OH)_2$; the latter remains in the

residue. The product is filtered, using the device shown in Fig. 52, p. 74, and washed with some alcohol. It contains some NaOH and $Ba(OH)_2$.

ANALYSIS:

The compound is disproportionated in acetic acid. The leached-out Re (VII) fraction is filtered off and precipitated with nitron; the Re (IV) fraction is oxidized to Re (VII) and also precipitated with nitron.

PROPERTIES:

Formula weight 387.58. Foliage-green powder; readily dissociated. Slowly turns black in vacuum and white in air (formation of ReO_4^-). Instantaneously dissociated by water, acids and bases. The presence of a slight amount of free NaOH is required for stability.

REFERENCE:

I. and W. Noddack. Z. anorg. allg. Chem. 215, 143 (1933).

Rhenium (IV) Sulfide

ReS_2

I.

$$\underset{186.2}{Re} + \underset{64.1}{2S} = \underset{250.3}{ReS_2}$$

Rhenium and sulfur are mixed in stoichiometric proportions and heated for 18 hours in an evacuated, sealed small quartz tube at 980–1000°C.

II. Hydrogen sulfide is used to precipitate Re_2S_7 from a hydrochloric acid solution; the precipitate is filtered off with suction and washed with water and briefly with acetone. It is dried in a quartz or hard glass tube sealed at one end. It is then heated in high vacuum to 600°C until no further S sublimes out. The result is ReS_2 only slightly contaminated with sulfur.

Alternate method: Heating of Re in a stream of H_2S to red heat [H. V. A. Briscoe, P. C. Robinson and E. M. Stoddart, J. Chem. Soc. (London) 1931, 1441].

PROPERTIES:

Black solid (platelets are seldom recognizable); somewhat volatile at 1000°C. Strongly attacks quartz at 1000°C. No appreciable solubility in bases, alkaline sulfides, hydrochloric and sulfuric

acids. Converted by oxidizing agents to $HReO_4$. d_4^{20} 7.506; heat of formation: −70.5 kcal. Crystal structure: C7 type.

REFERENCES:

I. R. Juza and W. Biltz. Z. Elektrochem. 37, 499 (1931).
II. W. Geilmann and G. Lange. Z. analyt. Chem. 126, 321 (1953).

Rhenium (VII) Sulfide

Re_2S_7

$$\underset{578.6}{2\,KReO_4} + \underset{155.0\ l.}{7\,H_2S} + \underset{72.9}{2\,HCl} = \underset{596.9}{Re_2S_7} + \underset{149.1}{2\,KCl} + 8\,H_2O$$

A solution of $KReO_4$, containing 30 ml. of hydrochloric acid per 100 ml. of solution, is saturated for four hours with H_2S. The precipitated sulfide is washed with H_2S-saturated, 3% HCl water. The product is filtered in the absence of air, washed and then dried, first in a high vacuum for two hours at 140°C and then in high vacuum over freshly prepared P_2O_5 (60 hours at 165–170°C).

Alternate method: Precipitation with compressed H_2S from a solution of $KReO_4$ in hydrochloric acid; there is no need for the high HCl concentration in this case. The workup is similar to that described above [W. Geilmann, Z. analyt. Chem. 126, 321 (1943)].

PROPERTIES:

Black, readily oxidized powder. Dissociation to ReS_2 and S begins at 250°C. Insoluble in hydrochloric and sulfuric acids in the absence of air; oxidized by nitric acid or H_2O_2 plus a base to $HReO_4$. d_4^{25} 4.866.

REFERENCE:

W. Biltz and F. Weibke. Z. anorg. allg. Chem. 203, 4 (1931).

Barium Mesoperrhenate

$Ba_3(ReO_5)_2$

Prepared by fusion of $Ba(ReO_4)_2$ with NaOH. The apparatus is the same as used in the preparation of Na_3ReO_5 (Fig. 329).

Crucible *c* is used to fuse 3 g. of $Ba(ReO_4)_2$ with 5 g. of carbonate-free NaOH under a stream of CO_2-free air. The hot melt is red and cloudy. After cooling, it is crushed, leached with 90% alcohol to remove the excess NaOH and the $NaReO_4$ formed in the process, then filtered, again washed with alcohol and dried with suction.

ANALYSIS:

The salt is decomposed with CO_2-free water; the Ba is precipitated as $BaSO_4$ and the ReO_4^- as nitron hydrogen perrhenate.

PROPERTIES:

Formula weight 944.52. Small, lemon-yellow hexagonal tablets and columns. Turns red upon heating to 800°C, returns to yellow on cooling. Stable in dry air. The wet salt is decomposed by CO_2 into $BaCO_3$ and $Ba(ReO_4)_2$.

REFERENCE:

I. and W. Noddack, Z. anorg. Chem. 215, 146 (1933).

Workup of Rhenium Residues

Precipitates of nitron hydrogen perrhenate from analyses of rhenium are collected and stored separately from rhenium solutions.

Workup of nitron precipitates: The material is carefully decomposed in a stream of H_2, the products washed and oxidized to Re_2O_7, and the latter dissolved in H_2O and concentrated in the presence of KOH or ammonia. The $KReO_4$ or NH_4ReO_4 obtained in this manner can be used without further purification.

Workup of various solutions: To avoid unnecessary contamination of the air with Re, the solution is neutralized and concentrated (if necessary, by boiling). It is then cooled and acidified with hydrochloric acid and the Re precipitated under pressure as Re_2S_7. The Re_2S_7 is washed and dissolved in KOH + H_2O_2, and the $KReO_4$ is allowed to crystallize out. If the $KReO_4$ is still not sufficiently pure, it is reduced with H_2 and oxidized with O_2 to Re_2O_7, and the latter is used to obtain Re or the perrhenate.

If traces of Mo must be removed, the procedure is as follows: the Re is precipitated with H_2S (under pressure) as Re_2S_7, the precipitate is dissolved in KOH + H_2O_2, and the traces of Mo

are removed by extraction of the neutral solution with 8-hydroxyquinoline or chloroform. Following repeated precipitation under pressure as Re_2S_7, the product is dissolved in KOH + H_2O_2 and crystallized as $KReO_4$. The $KReO_4$ is recrystallized from hot water.

DropBooks

SECTION 27

Iron

H. LUX

Metallic Iron

ELECTROLYTIC IRON

The following conditions are suitable for the preparation of very pure electrolytic iron: each liter of electrolyte contains about 800 g. of very pure $FeCl_2 \cdot 4H_2O$ (Fe^{3+} content less than 0.05%; sulfate-free) and 1.5–2.0 g. of $AlCl_3 \cdot 6H_2O$ or 0.1 g. of $CrCl_3 \cdot 6H_2O$. The concentration of free HCl is 0.01–0.02 N, and the temperature is 90°C or higher. The anode is made of the purest iron possible, and is wrapped in an asbestos bag. A sheet of vanadium steel serves as the cathode. The nature of cathode pretreatment is important if the deposit of electrolytic iron is to be easily stripped off. The steel sheet is first polished to a high luster, degreased by being used as a cathode in an alkaline KCN bath, rinsed with water, and after being connected to the electrical circuit, placed in a $FeCl_2$ bath. The cathodic density is 0.65–1.0 amp./in.^{2}; if the operation is of long duration or proceeds at still higher current densities (up to 2 amp./ in.^{2}), the electrolyte must be continuously taken out of the bath, filtered, retreated, the HCl content adjusted to the one indicated above, and recycled to the bath.

The relatively soft α-iron deposited contains H_2 but no Al or Cr. The H_2 may be completely removed by baking in vacuum at 950°C. Electrolytic iron is free of C or Si, and of other metals if the electrolyte itself is pure.

PROPERTIES:

M.p. 1535°C, b.p. 2730°C; d 7.86. Crystal structure of α-Fe: A 2 type.

REFERENCES:

G. A. Moore. J. Metals 5, 1443 (1953); F. Müller. Z. Elektrochem. 47, 135 (1941); F. Halla. Korrosion und Metallschutz 15, 380 (1939).

REDUCED IRON

$$\underset{213.7}{2\,Fe(OH)_3} + \underset{67.2\,l.}{3\,H_2} = \underset{111.7}{2\,Fe} + \underset{108.1}{6\,H_2O}$$

It is best to start from very pure $Fe(OH)_3$; this is prepared by adding a $Fe(NO_3)_3$ solution to aqueous NH_3 and drying the precipitate at 65°C. The product, finely ground, is placed in an aluminum or Pt boat (with Pt foil insert) and reduced in a stream of H_2 as the temperature is slowly raised. If the reduction temperature is lower than 550°C, the iron product is pyrophoric. As a rule, the temperature is raised slowly from 400 to 700°C (with 20 g. of Fe_2O_3, this requires about 40 min.) and then held constant (about 20 min.) until further H_2O is produced. If less reactive starting materials (e.g., Fe_2O_3 prepared from the nitrate) are used, it may be necessary to heat to higher temperatures (1050–1100°C) and for much longer times (60 hours or more) to insure complete reduction. The preparations are cooled in H_2; their hydrogen content is minimal.

REFERENCES:

R. Fricke and L. Klenk. Z. Elektrochem. 41, 617 (1935); R. Fricke, O. Lohrmann and W. Wolf. Z. phys. Chem. (B) 37, 60 (1937); P. M. Savelevich. Trudy Inst. Chist. Khim. Reaktivov, No. 15, 51 (1937); abstract in Chem. Zentr. 1939, I, 4563; G. P. Baxter and C. R. Hoover. Z. anorg. allg. Chem. 80, 211 (1913).

VERY PURE IRON:

O. Hönigschmid, L. Birckenbach and R. Zeiss. Ber. dtsch. chem. Ges. 56, 1473 (1923); T. W. Richards and G. P. Baxter. Z. anorg. Chem. 23, 247 (1900); also A. Gatterer. Commentationes Pontific. Acad. Sci. 1, 77 (1937); abstract in Chem. Zentr. 1938, I, 1745; A. Gatterer and J. Junkes. Specola astronom. Vaticana Comun. No. 6 (1938); abstract in Chem. Zentr. 1938, II, 2243; J. Talbot, P. Albert, M. Caron and G. Chaudron. Rev. Met. 50, 817 (1953).

Iron (II) Chloride

$FeCl_2$

$$\underset{55.8}{Fe} + \underset{33.6\,l.}{{}^3/_2\,Cl_2} = \underset{162.2}{FeCl_3};\quad \underset{162.2}{FeCl_3} + \underset{11.2\,l.}{{}^1/_2\,H_2} = \underset{126.8}{FeCl_2} + \underset{36.5}{HCl}$$

The starting anhydrous $FeCl_3$ is prepared from Fe and Cl_2. The Cl_2 is then displaced by means of a stream of very dry N_2, and

completely dry, pure H_2 is immediately introduced. The reduction proceeds rapidly at 300-350°C. It is advisable to spread the solid in a tube placed in a long electric furnace and to heat slowly, section by section, in the H_2 stream. Partly unconverted $FeCl_3$ sublimes in the H_2 below 300°C, while above 350°C the $FeCl_3$ tends to be reduced too far (to Fe).

The preparation of $FeCl_2$ from Fe and HCl is less satisfactory because of the higher temperatures required.

SYNONYMS:

Ferrous chloride, iron dichloride.

PROPERTIES:

White hygroscopic powder; can be resublimed in a stream of HCl at about 700°C. M.p. 674°C, b.p. 1023°C; d (25°) 3.162. Vapor pressure at 700°C: 12 mm. Readily soluble in water and alcohol. Crystal structure: C 19 type.

REFERENCES:

H. Wolfram. Thesis, Techn. Hochschule Dresden, 1913; W. Kangro and E. Petersen. Z. anorg. allg. Chem. 261, 157 (1950).

Iron (III) Chloride

$FeCl_3$

$$2\,Fe + 3\,Cl_2 = 2\,FeCl_3$$
$$111.7 \quad 67.2\,l. \quad 324.4$$

A stream of Cl_2 is very thoroughly dried over conc. H_2SO_4 and P_2O_5, and is then liquefied by passage through a U tube cooled with Dry Ice-acetone mixture to about −40°C. The bath temperature is then raised to −34.1°C; pure Cl_2 volatilizes out. It passes into a very dry Pyrex tube containing the purest possible iron wire (about 0.2 mm. in diameter). The reaction takes place at 250-400°C; an excess of Cl_2 should always be present and should always bubble out from the H_2SO_4-containing safety valve which terminates the reactor train. To avoid plugging the tube, the electric furnace (or the aluminum heating block) is occasionally shifted, so that a fresh condensation zone may be created.

At the end of the reaction, the preparation should be resublimed in a stream of Cl_2 at about 220°C (the temperature should

not exceed 300°C). All of the Cl_2 is then displaced from the apparatus with very dry N_2 (or air), and the product is transferred (under N_2) to storage vessels, which are then tightly sealed.

SYNONYMS:

Ferric chloride; iron trichloride.

PROPERTIES:

Formula weight 162.2. Leaflets with a somewhat greenish metallic luster. Extremely hygroscopic. M.p. (in Cl_2) 308°C, b.p. (calcd.) 316°C; d (25°) 2.898. Decomposes partially on sublimation in high vacuum. In the range of 160-210°C the decomposition pressure of Cl_2 over solid $FeCl_3$ and $FeCl_2$ obeys the equation: $\log P = 11.33 - 5.67 \cdot 10^3/T$. Very readily soluble in water, ethyl alcohol, ethyl ether and acetone. $FeCl_3$ and $FeCl_2$ form a eutectic, m.p. 297.5°C, containing 13.4 mole % of $FeCl_2$.

REFERENCES:

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G. G. Maier. Techn. Pap. Bur. Mines Washington No. 360, 40 (1925); O. Hönigschmid, L. Birckenbach and R. Zeiss. Ber. dtsch. chem. Ges. 56, 1476 (1923); H. Schäfer. Angew. Chem. 64, 111 (1952); for the preparation of larger amounts, see B. R. Tarr in: L. F. Audrieth, Inorg. Syntheses, Vol. III, New York, 1950, p. 191.

Iron (II) Bromide

$FeBr_2$

$FeBr_2$, ANHYDROUS

I.

$$\underset{55.9}{Fe} + \underset{161.8}{2\,HBr} = \underset{215.7}{FeBr_2} + \underset{22.4\,l.}{H_2}$$

Very pure Fe (reduced with H_2) is placed in an unglazed porcelain boat situated in a porcelain tube and heated to about 800°C in a completely dry stream of HBr-saturated nitrogen, so that the nascent $FeBr_2$ distills out at once. The preparation is transferred (in dry N_2) to well-sealed vessels. This last operation is facilitated by attaching a snugly fitting tube onto the exit end of the reactor; the $FeBr_2$ can then sublime into this second tube.

B. Careful dehydration of $FeBr_2 \cdot 4H_2O$ in a stream of N_2 and HBr.

SYNONYM:

Ferrous bromide.

PROPERTIES:

Light-yellow to dark-brown crystals; hygroscopic. M. p. 684°; d (25°) 4.624. Crystal structure: C 6 type.

REFERENCES:

I. G. P. Baxter. Z. anorg. Chem. 38, 236 (1904).
II. G. P. Baxter, Th. Thorvaldson and V. Gobb. Z. anorg. Chem. 70, 333 (1911).

$FeBr_2$. HYDRATE

$$\underset{55.9}{Fe} + \underset{161.8}{2\,HBr} - \underset{}{6\,H_2O} = \underset{323.8}{FeBr_2 \cdot 6\,H_2O} + \underset{}{H_2}$$

To prepare the hexahydrate, pure iron is dissolved in aqueous HBr and the solution evaporated below 49°C. Above this temperature one can obtain the tetrahydrate, and above 83°C the dihydrate.

Alternate method: Shaking Br_2 and water with an excess of iron powder.

PROPERTIES:

Pale-green rhombic tablets; not deliquescent.

REFERENCE:

F. Schimmel. Ber. dtsch. chem. Ges. 62, 963 (1929).

Iron (III) Bromide

$FeBr_3$

$$\underset{111.7}{2\,Fe} + \underset{479.5}{3\,Br_2} = \underset{591.2}{2\,FeBr_3}$$

A Pyrex tube, sealed at the left end and provided with a 45° bend in the middle, is connected at the right to a high-vacuum pump and a supply of Br_2. Reduced iron powder is introduced into the left leg with the aid of a long-stem funnel, and the right end of the tube is then drawn out to a capillary. The Fe is thoroughly degassed by evacuation and heating. Bromine is then condensed on

the iron (liquid nitrogen bath); the Br_2 excess is such that after completion of the reaction the pressure in the tube will still be at least 5 atm.

After the pump end of the reactor tube is sealed off, the Br_2 is condensed in the right leg by cooling the latter in ice water. The left leg is then heated to 175–200°C (maximum) and then the right leg to 120°C; this produces a Br_2 pressure of about 5 atm. The heating is done with two mating aluminum heating blocks. The butting ends are cut at an angle of 22.5° and separated only by a thin disk of asbestos (Fig. 330).

The reaction begins, although slowly, even at room temperature, but cannot be completed at this temperature even in several months. However, under the conditions given above, pure $FeBr_3$ condenses outside the 200°C zone. If the temperature of the Fe is too high or the Br_2 pressure too low, some yellow $FeBr_2$ is also deposited at the left end of the tube.

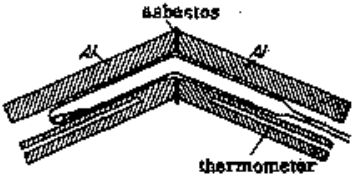

Fig. 330. Preparation of iron (III) bromide.

SYNONYM:

Ferric bromide.

PROPERTIES:

Lustrous black plates; very hygroscopic. The decomposition pressure of Br_2 at 90°C is 55 mm. and at 139°C is 760 mm.; below 139°C, it obeys the equation: log p (mm.) = $-3478.6/T + 11.327$. The vapor pressure of $FeBr_3$ becomes detectable above 139°C. Crystal structure: $D0_5$ type (same as $FeCl_3$).

REFERENCES:

N. W. Gregory and B. A. Thackrey. J. Amer. Chem. Soc. 72, 3176 (1950); N. W. Gregory. Ibid. 73, 472 (1951).

Iron (II) Iodide

FeI_2

I. $Fe + I_2 = FeI_2$

55.8 253.8 309.7

A high-melting glass tube is sealed at one end and provided with a side arm terminating in a break-seal capillary d (see Fig. 331). Very pure iron wire is placed at location a of the tube, and a small plug of freshly ignited asbestos wool b is inserted close

to the iron. Pure, dry I_2 (less than stoichiometric quantity), in the form of a coarse powder, is then placed on top of the asbestos wool plug. The reactor tube is then drawn out to smaller size at *a*, the I_2 is moved forward to *c*, and a good vacuum is applied by means of a mercury diffusion pump. At the same time, the other sections of the tube (*a*, *b*) are heated in an electric furnace to 500°C to degas the Fe and the asbestos. The tube is then sealed off at *f*, and section *c* containing the I_2 is heated to 180°C with a suitable Al block or in an air bath (the section containing the Fe is maintained at 500°C). The tube is slightly inclined forward to prevent the liquid iodine from flowing into the hot section. If the above temperatures are adhered to, the internal pressure does not exceed one atmosphere.

The nascent FeI_2 sublimes slowly toward the cooler zone, where it deposits as black leaflets which appear brownish red when viewed by transmitted light. As soon as the iodine vapor disappears completely, the tube is allowed to cool and a vacuum hose is carefully slipped over side arm *d*. The hose is connected via a three-way stopcock to a canned-rotor pump and a nitrogen supply. Vacuum is applied, the sealed capillary on the side arm is broken off, and pure, dry N_2 is slowly admitted. Care should be taken during this step to avoid entraining any glass fragments in the tube. As soon as a slight gage pressure is established, the reactor tube is broken off at *e* and the product is transferred in nitrogen to a storage vessel.

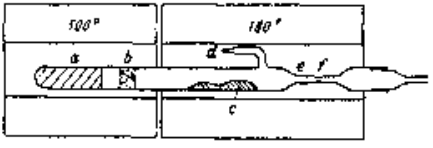

Fig. 331. Preparation of iron (II) iodide. *a* iron wire; *b* asbestos wool; *c* iodine; *f* seal location (after sealing, the section to the right of *f* is removed).

Alternate methods: II. Heating reduced Fe in a stream of I_2-saturated hydrogen, followed by distillation in a steel tube.

III. Thermal decomposition of $Fe(CO)_4I_2$. The product is an extremely fine powder.

SYNONYM:

Ferrous iodide.

PROPERTIES:

M. p. 587°. Hygroscopic; becomes whitish in air. Aqueous solutions are colorless. Crystal structure: C 6 type.

REFERENCES:

I. M. Guichard. Comptes Rendus Hebd. Séances Acad. Sci. 145, 807 (1907).
II. C. L. Jackson and I. H. Derby. Amer. Chem. J. 24, 16 (1900); Bull. Soc. Chim. France [3] 24, 863 (1900); see also W. Fischer and R. Gewehr. Z. anorg. allg. Chem. 222, 303 (1935).
III. W. Hieber and H. Lagally. Ibid. 245, 300, 313 (1940).

Iron (II) Oxide

FeO

I. $$\underset{143.8}{FeC_2O_4} = \underset{71.8}{FeO} + \underset{28.0}{CO} + \underset{44.0}{CO_2}$$

Thermal decomposition of FeC_2O_4 yields pure FeO only under specific conditions. The decomposition is carried out in a quartz vessel (Fig. 332) whose lower section is kept at 850°C by means of an electric furnace. The joint is surrounded by a water-cooled lead coil or a rubber hose. The nascent gases should be removed as quickly as possible; for this reason, the reactor is connected to two parallel mercury pumps and a good forepump; the gas is carried into two liquid-nitrogen-cooled traps containing activated charcoal.

The starting FeC_2O_4 (0.5–0.8 g.) is placed in the small bulb above the quartz vessel, and the water of crystallization is completely vaporized by heating in vacuum for 12 hours at 200°C. The bulb is turned in the joint, and the FeC_2O_4 drops into the heated lower section of the reactor where it is rapidly decomposed to FeO, CO and CO_2 (the decomposition is complete in about 20 seconds). The product FeO is retained by a quartz wool plug, which must be loose enough to prevent a buildup of pressure during the decomposition.

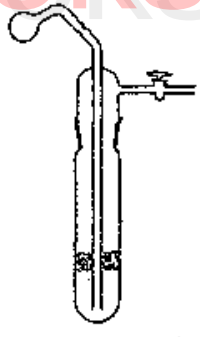

Fig. 332. Preparation of iron (II) oxide.

The furnace is now removed and the hot quartz tube is chilled as rapidly as possible in cold water, since FeO is unstable in the range of 300–560°C and decomposes according to:

$$4FeO = Fe_3O_4 + Fe$$

(this decomposition proceeds most rapidly at about 480°C, but ceases below 300°C). The above procedure yields a jet-black

product, readily soluble in dilute acids; it is rapidly oxidized in air, but does not ignite.

II. The preparation from stoichiometric quantities of commercial Fe_2O_3 and reduced iron can also be recommended. The mixture and a few drops of water are sealed into a preevacuated quartz tube, heated for about three days at 900°C, and quenched in cold water.

SYNONYM:

Ferrous oxide.

PROPERTIES:

M.p. 1360°; d 5.7. Crystal structure: B1 (rock salt) type.

REFERENCES:

I. P. L. Günther and H. Rehaag. Z. anorg. allg. Chem. 243, 60 (1939).

II. R. W. Blue and H. H. Claassen. J. Amer. Chem. Soc. 71, 3839 (1949); J. P. Coughlin, E. G. King and K. R. Bonnickson, ibid. 73, 3891 (1951); see also L. Wöhler and R. Günther. Z. Elektrochem. 29, 281 (1923).

Iron (II) Hydroxide

$Fe(OH)_2$

The preparation of pure $Fe(OH)_2$ has been described in detail by Rihl and Fricke as an example of operation under an inert atmosphere. The general experimental arrangement is further described in Part I, p. 72 ff. It consists essentially of a bulb, one side of which can be connected to a high-vacuum pump as well as a source of N_2 or a drying vessel, while the other side is attached to devices for filtration, washing and transfer of products. All operations must be carried out with the most rigorous exclusion of O_2 in an atmosphere of pure, dry N_2.

The apparatus is first evacuated (high vacuum); then a continuous stream of N_2 is introduced. A centrifuged solution of $Fe(OH)_2$ (prepared from very pure $FeCl_2$) in conc. aqueous NH_3 is admitted through the filter and diluted with a large quantity of water, causing precipitation of the $Fe(OH)_2$. To obtain a denser precipitate (which settles more rapidly), the mixture is heated for about three hours at 80°C and allowed to settle. The mother liquor is filtered off, and the precipitate is washed 10 to 12 times in similar fashion until a positive test for chloride is no longer obtained.

To remove the remaining water, the residue is solidified by immersion of the flask in an ice–salt mixture, full vacuum is applied, and the water is distilled off overnight as the solid slowly melts. The water is condensed in a large trap chilled in Dry Ice–acetone. Complete drying of the product is achieved by keeping it for several additional hours under high vacuum together with a vessel containing P_2O_5.

PROPERTIES:

Nearly white, slight greenish tinge. When sprayed into air, burns with sparks. Crystal structure: C 6 type.

REFERENCE:

S. Ribl and R. Fricke, Z. anorg. allg. Chem. 251, 406 (1943).

Iron (II, III) Oxide

Fe_3O_4

$$\underset{479.0}{3\,Fe_2O_3} + \underset{22.41.}{H_2} = \underset{463.0}{2\,Fe_3O_4} + \underset{18.0}{H_2O}$$

Fine Fe_2O_3 powder is heated to 400°C in a large boat placed in a stream of N_2; then the N_2 is replaced with H_2 saturated with water vapor at 50°C. The connecting tubing between the saturating vessel and the reactor tube must be as short as possible and well insulated against thermal losses. When the reduction is complete, as shown by the disappearance of all of the red Fe_2O_3, the product is cooled in a stream of N_2. Conversion of 10 g. of Fe_2O_3 requires about five hours.

PROPERTIES:

Black, ferromagnetic powder. M.p. 1590°; d 5.11. Mohs hardness 6. Crystal structure: H 11 type.

REFERENCE:

S. Hilpert and J. Beyer, Ber. dtsch. chem. Ges. 44, 1608 (1911).

Iron (III) Hydroxide

FeO(OH)

α-FeO(OH)

$$\underset{404.0}{Fe(NO_3)_3 \cdot 9\,H_2O} + \underset{51.1}{3\,NH_3} = \underset{88.9}{FeO(OH)} + \underset{240.2}{3\,NH_4NO_3} + 7\,H_2O$$

A cold solution of 810 g. of $Fe(NO_3)_3 \cdot 9\,H_2O$ in two liters of water is poured slowly, with vigorous stirring, into an ammonia

solution prepared by dissolving 120 g. of gaseous NH_3 in two liters of water (cooling necessary). The hydroxide which precipitates is amorphous to x-ray analysis. It is washed by stirring at least five times with eight-liter portions of cold water, each portion being decanted as completely as possible. The residual slurry is then stirred with sufficient conc. KOH solution to give a mixture approximately 2N and allowed to stand for 3-4 hours. Finally 100°C steam is bubbled through for two hours. The precipitate is thereby transformed completely into bright-yellow α-FeO(OH), which shows a crystalline x-ray diffraction pattern.

Since removal of the potassium hydroxide by washing is difficult, it is converted to KCl by treatment with somewhat more than the calculated amount of NH_4Cl. The precipitate is then washed thoroughly with hot water until no further Cl^- can be detected. The K content is then usually below 0.04%. Drying in a vacuum desiccator affords a product whose water content still exceeds the theoretical (10.14%) by about 2%. Heating in vacuum or in a stream of dry air yields pure α-Fe_2O_3.

The naturally occurring form of α-FeO(OH), "needle iron ore" or goethite, has an EO_2 type structure.

REFERENCES:

R. Fricke and P. Ackermann. Z. Elektrochem. 40, 630 (1934); O. Glemser. Ber. dtsch. chem. Ges. 70, 2117 (1937); R. Fricke and G. F. Hüttig. Hydroxyde und Oxydhydrate [Hydroxides and Hydrated Oxides], Leipzig, 1937, p. 316; W. Hoppe. Z. Kristallogr. (A) 103, 73 (1940).

γ-FeO(OH)

$$2\,FeCl_2 \cdot 4\,H_2O + (CH_2)_6N_4 + 2\,H_2O = 2\,Fe(OH)_2 + 4\,NH_4Cl + 6\,H_2O$$
$$397.8 \qquad 140.1 \qquad 36.0 \qquad 179.7 \qquad 214.0 \qquad 108.1$$

$$Fe(OH)_2 + NaNO_2 + HCl = FeO(OH) + NO + NaCl + H_2O$$
$$89.9 \qquad 69.0 \qquad 36.5 \qquad 88.9 \qquad 30.0 \qquad 58.5 \qquad 18.0$$

A solution of 120 g. of $FeCl_2 \cdot 4\,H_2O$ in three liters of water is filtered, and the filtrate is added to a filtered solution of 168 g. of hexamethylenetetramine (Urotropin) in 600 ml. of water. Blue-green $Fe(OH)_2$ is precipitated. Then a solution of 42 g. of $NaNO_2$ in 600 ml. of water is added with constant stirring; the mixture is heated to about 60°C and allowed to stand three hours (not longer) with occasional agitation. The oxidation, which produces γ-FeO(OH), proceeds with the evolution of considerable quantities of nitrogen oxides. The supernatant liquid is drained off; the precipitate is washed thoroughly with warm water until free of chloride and dried at 60°C in a drying oven.

PROPERTIES:

Very friable deep-orange powder comprised of extremely fine needles. Can be converted to pure γ-Fe_2O_3 by heating in vacuum or in a dry air stream at about 250-400°C. On heating at higher temperatures, or in a sealed tube at 110°C, or even on very intensive grinding, the metastable preparations of the γ series are converted to the stable α modification.

Occurs in nature as lepidocrocite. Crystal structure: $E0_4$ type. For metastable δ-FeO(OH), see O. Kratky and H. Nowotny, Z. Kristallogr. (A) 100, 356 (1938).

REFERENCES:

O. Glemser, Ber. dtsch. chem. Ges. 71, 158 (1938); R. Fricke and W. Zerrweck, Z. Elektrochem. 43, 52 (1937); R. Fricke and G. Weitbrecht, Z. anorg. allg. Chem. 251, 427 (1943); F. Wagenknecht, Kolloid-Z. 112, 35 (1949).

Iron (III) Oxychloride

FeOCl

$$FeCl_3 \cdot 6H_2O + 5FeCl_3 = 6FeOCl + 12HCl$$
$$270.3 \quad 811.1 \quad 643.8 \quad 87.6$$

A mixture of 10 g. of $FeCl_3 \cdot 6H_2O$ and 35 g. of sublimed $FeCl_3$ is placed in a round, short-neck Pyrex reaction flask, fused on a steam bath, and allowed to solidify; then 15 additional g. of $FeCl_3$ is added. The reaction indicated above takes place when the mass is heated to 250-300°C (maximum). It is best to immerse the open flask rather deeply in an oil bath held at 250°C, so that no moisture condenses at the neck. The reaction is complete after 60-80 minutes, when no further evolution of HCl is observed.

The reaction mass, which converts to a solid red cake, is cooled and pulverized, washed briefly with a large amount of cold water and then with acetone (to remove excess $FeCl_3$), and dried in vacuum.

PROPERTIES:

Rust-colored powder consisting of small red needles. Free of Fe_2O_3 if made from sublimed $FeCl_3$ and if reaction temperatures no higher than 300°C are used. Disproportionates above 300°C into the oxide and chloride. Crystal structure: $E0_8$ type.

REFERENCE:

H. Schäfer, Z. anorg. Chem. 260, 279 (1949).

DropBooks

Iron (II) Sulfide

FeS

$$\underset{55.8}{Fe} + \underset{32.1}{S} = \underset{87.9}{FeS}$$

Pure FeS of stoichiometric composition is obtained from pure reduced Fe and distilled S. Exactly weighed quantities of the two substances are sealed in a quartz tube evacuated in high vacuum, and are heated for about 24 hours at 1000°C; at higher temperatures, the quartz tube bursts. One then tests for completeness of the conversion: the reaction is complete if S no longer collects at that end of the hot tube which is cooled for test purposes. The lustrous gray product obtained is somewhat sintered and readily pulverized.

SYNONYM:

Ferrous sulfide.

PROPERTIES:

M. p. 1195°; d 4.84. Crystal structure: B 8 type.

REFERENCES:

H. Haraldsen. Z. anorg. allg. Chem. 231, 81 (1937); G. Hägg and J. Sucksdorff. Z. phys. Chem. (B) 22, 444 (1933).

Iron Nitrides

Fe_2N, Fe_4N

I.
$$\underset{223.4}{4\,Fe} + \underset{44.8\,l.}{2\,NH_3} = \underset{251.4}{2\,Fe_2N} + \underset{67\,l.}{3\,H_2}$$

Fine Fe_2O_3 powder is placed in a porcelain boat at 500°C and reduced as completely as possible with H_2; then, without allowing any air to penetrate, NH_3 is introduced at 350–550°C until the H_2 content of the exit gas decreases to a low, constant level. The product is then allowed to cool in the stream of NH_3. It corresponds in composition to the formula Fe_2N (theoretically 11.1% N), has the structure of Hägg's ζ phase, and exhibits a very narrow region of homogeneity. Often, however, the same composition yields a mixed crystal (solid solution) phase ϵ. On heating in vacuum at about 500°C the product is converted (with loss of N_2) first to the solid solution ϵ and then to Fe_4N (γ' phase, theoretically 5.9% N).

II. Another method for preparing Fe_4N consists in heating reduced iron in the presence of an appropriate mixture of H_2 and NH_3.

PROPERTIES:

Fe_2N: Formula weight 125.7; d 5.02.

Fe_4N: Formula weight 237.4; d 6.57 (?). Crystal structure: L 1$_0$ type.

REFERENCES:

I. G. Hägg. Z. phys. Chem. (B) 8, 455 (1930); also E. Lehrer. Z. Elektrochem. 36, 388, 460 (1930); O. Eisenhut and E. Kaupp. Ibid. 36, 394 (1930); S. Satoh. Bull. Chem. Soc. Japan 7, 315 (1932); abstract in Chem. Zentr. 1933, I, 752.

II. St. Brunauer, M. E. Jefferson, P. H. Emmett and S. B. Hendricks. J. Amer. Chem. Soc. 53, 1778 (1931); Ch. Guillaud and H. Creveaux. Comptes Rendus Hebd. Séances Acad. Sci. 222, 1170 (1946); H. W. Kohlschütter and M. Pavel. Z. anorg. allg. Chem. 255, 65, 73 (1947).

Iron Carbide

Fe_3C

It is best to start with electrolytic iron sheet; this is held over benzene vapor to deposit a layer of carbon, then baked for a long time in vacuum at 700°C and slowly cooled. To isolate Fe_3C the sheet is placed in a neutral $FeCl_2$ bath and used as an anode at the lowest possible current density. The bath is the same as used in the preparation of electrolytic iron. In this way very pure Fe_3C is left behind as a coarsely crystalline gray powder. It is washed with dilute acetic acid, water, alcohol and ether, and dried in vacuum.

Alternate methods: *a*) Iron carbide may also be isolated quantitatively while measuring the anode potential; see E. Houdremont, P. Klinger and G. Blaschczyk, Techn. Mitt. Krupp, Forschungsber. 4, 311; Arch. Eisenhüttenw. 15, 257 (1941).

b) Solution of white, low-Si pig iron in 1 N acetic acid; see O. Ruff and E. Gersten, Ber. dtsch. chem. Ges. 45, 64 (1912).

c) For the preparation of almost pure fused Fe_3C, see F. Wever, Mitt. KWI Eisenforschung 4, 67 (1923).

SYNONYM:

Cementite.

PROPERTIES:

Formula weight 179.52. Hardness 3.2–3.3; d (15°) 7.66. Crystal structure: D0$_{11}$ type.

The decomposition of Fe_3C to Fe and C proceeds at a high rate only above 1060°C. Below 500°C a carbide having the formula Fe_2C may also be obtained in various modifications [L. J. E. Hofer, E. M. Cohn and W. C. Peebles, J. Amer. Chem. Soc. 71, 189 (1949); H. H. Podgurski, J. T. Kummer, T. W. de Witt and P. H. Emmett, ibid. 72, 5382 (1950)].

REFERENCE:

G. Naeser. Mitt. KWI für Eisenforschung 16, 211 (1934).

Lithium Ferrate (III)

$LiFeO_2$

Obtained by heating to high temperature or fusion of an intimate mixture of Li_2CO_3 with fine Fe_2O_3 powder derived from FeC_2O_4. At temperatures above about 670°C, the stable modification is of the B1 type, with random distribution of the metal atoms; annealing at 570°C converts it to a nearly cubic tetragonal modification with ordered distribution.

Alternate method: Heating conc. LiOH solution with Fe_2O_3 at 600°C under pressure [E. Posniak and T. F. W. Barth, Phys. Rev. 38, 2234 (1931)].

REFERENCE:

F. Barblan, E. Brandenberger and P. Niggli. Helv. Chim. Acta 27, 88 (1944).

Potassium Ferrate (VI)

K_2FeO_4

I. BY OXIDATION WITH NaOCl:

$$\underset{80.0}{2\,NaOH} + \underset{70.9}{Cl_2} = \underset{58.5}{NaCl} + \underset{74.5}{NaOCl} + H_2O$$

$$\underset{223.5}{3\,NaOCl} + \underset{808.0}{2\,Fe(NO_3)_3 \cdot 9\,H_2O} + \underset{400.0}{10\,NaOH} =$$

$$\underset{331.7}{2\,Na_2FeO_4} + \underset{510.0}{6\,NaNO_3} + \underset{175.5}{3\,NaCl} + 23\,H_2O$$

$$\underset{165.9}{Na_2FeO_4} + \underset{112.2}{2\,KOH} = \underset{198.0}{K_2FeO_4} + \underset{80.0}{2\,NaOH}$$

A solution of 30 g. of NaOH in 75 ml. of water is cooled, and Cl_2 is admitted with vigorous stirring until a weight increase of

20 g. is recorded. The cooling rate should be such that the mixture temperature does not rise above 20°C. Then 70 g. of solid NaOH is added slowly and with constant stirring; the temperature is allowed to rise to 25–30°C to speed the dissolution. As soon as this is complete, the solution is cooled once again to 20°C and passed through a glass filter to remove the precipitated NaCl.

With the NaOCl solution held at 25–30°C, 25 g. of solid $Fe(NO_3)_3 \cdot 9H_2O$ is slowly added (stirring), the mixture is saturated with solid NaOH at 30°C, and the ferrate (VI) solution is either filtered through a coarse glass filter or, better, centrifuged.

The precipitation of K_2FeO_4 is carried out in a 250-ml. beaker by addition of 100 ml. of saturated KOH while stirring and cooling to 20°C. After precipitation, stirring is continued for five minutes; the compound is collected on a medium-porosity glass filter and redissolved by treatment with four or five 10-ml. portions of 3 M KOH. The solutions are combined in a 250-ml. beaker and 50 additional ml. of saturated KOH is added; after five minutes of stirring at 20°C the solution, which is now about 11 M in KOH, is filtered through a medium-porosity glass filter.

For further purification, the K_2FeO_4 collected on the filter is treated with 10 ml. of benzene, then three to five times with 20-ml. portions of 95% ethanol (aldehyde-free), and finally stirred for 20 min. (in a large beaker) with 1000 ml. of 95% ethanol. This last treatment is repeated three additional times. The product is collected on a glass filter, washed in the absence of atmospheric moisture with 50 ml. of ether, and dried in a vacuum desiccator.

The yield is 45–75% of theoretical, the purity 92–96%. One further reprecipitation from 6 M KOH raises the purity to 98.5–99%.

II. ELECTROLYTIC METHOD:

$$\underset{55.85}{Fe} + 8\,KOH = \underset{198.0}{K_2FeO_4} + 6K^+ + 4H_2O + 6e^-$$
$$\qquad\qquad\quad \underset{448.8}{}$$

The electrolysis is conducted in a cylindrical vessel (95 mm. I. D. and 100 mm. high) in which a porous clay cell (50 mm. I. D. and 80 mm. high) is set. The cell is held in place by a paraffin-soaked cork ring in such a way that it touches the bottom of the cylinder. The anode is a strip of transformer iron sheet (0.3% Mn; 27 × 3.7 cm. = 100 cm.^{2} of surface on each side) which adheres closely to the outer wall. The cathode consists of a screen of iron wire rolled into a cylinder and placed inside the cell. The anode is welded to a thick, acetylene-flame-cleaned iron wire, which passes through the cork ring and is sealed in

with picein wax. The cork ring also carries a thermometer, a two-bulb pressure release tube containing 30% KOH, and a short tube (7 mm. I. D.) for removing samples.

Both cathode and anode are etched with 1:1 HCl shortly before the start of the experiment, and are then rinsed with water. The cylinder is now filled with 200 ml. and the cell with 60 ml. of freshly prepared 40% NaOH precooled to 25-28°C. The apparatus is assembled and cooled externally with ice water. To start with, the electrode intended as the anode is connected as the cathode and the electrolysis conducted for 3-5 min. at 3.5 amp. and 110 v. d.c. The resistance in the circuit should be about 30 ohms. The polarity is then reversed; the actual electrolysis takes four hours at 4.5 amp. (approximately 5.8 v.); the temperature in the anode space must never exceed 35°C.

The current is shut off and the anode electrolyte freed of traces of $Fe(OH)_3$ by centrifuging or filtering rapidly through a medium-porosity glass filter. The filtrate is cooled to 10°C, and 75 g. of KOH pellets is added with continued cooling and vigorous shaking. An additional hour at 0°C is allowed for completion of the reaction. The K_2FeO_4 precipitate is rapidly collected on a medium-porosity glass funnel, washed at once with ice-cold absolute methanol, and dried in vacuum over P_2O_5. The anode electrolyte, which after four hours is about 0.15 *M* in ferrate (VI), affords about 5 g. of K_2FeO_4 with a purity of 95%. The main impurity is carbonate; in addition there is 0.1% Mn, as well as compounds passing into the solution from the earthenware cell. These could probably be avoided by using a cell made of polytetrafluoroethylene or a similar material. The current efficiency is about 25%.

PROPERTIES:

Small lustrous crystals, very dark violet to black; stable only when completely dry. Readily soluble in water; concentrated solutions decompose rapidly; very dilute solutions are much more stable. Chloride ions and FeO(OH) markedly accelerate the decomposition. The instability of solutions as a function of pH is described by J. M. Schreyer and L. T. Ockerman, Anal. Chem. 23, 1312 (1951).

REFERENCES:

1. G. W. Thompson, L. T. Ockerman and J. M. Schreyer, J. Amer. Chem. Soc. 73, 1379 (1951); H. J. Hrostowski and A. B. Scott, J. Chem. Phys. 18, 105 (1950); B. Helferich and K. Lang, Z. anorg. Chem. 263, 171 (1950); R. Scholder, H. von Bunsen, F. Kindervater and W. Zeiss, Z. anorg. allg. Chem. 282, 268 (1955); L. Moeser, J. prakt. Chem. [2] 56, 431 (1897).

H. G. Grube and H. Gmelin. Z. Elektrochem. 26, 160 (1920); modified directions based on unpublished experiments made together with H. Noeth.

Potassium Iron (III) Sulfide

$KFeS_2$

$$6\,Fe + 4\,K_2CO_3 + 13\,S = 6\,KFeS_2 + K_2SO_4 + 4\,CO_2$$
$$335.0 \quad 525.8 \quad 416.5 \quad 954.4 \quad 174.3$$

An intimate mixture of 5 g. of Fe powder (obtained by reduction with H_2), 25 g. of K_2CO_3, 5 g. of Na_2CO_3, and 30 g. of S is slowly heated in a half-filled covered porcelain crucible until the mass flows smoothly; it is then held at bright-red heat for about one hour. A better method consists in heating the mixture (which is placed in a boat inserted in a porcelain tube) under nitrogen at 900–1000°C. In either case the crucible is cooled slowly and broken. The fragments of the melt are soaked in warm water, the solution being frequently decanted, until the only substance remaining in the flask is the reddish violet needles of $KFeS_2$ (semimetallic luster). If a considerable quantity of colloidal, amorphous product is obtained, the reaction temperature was not sufficiently high. The crystals are washed with water and alcohol and dried as rapidly as possible at 100°C. The yield is 12–14 g.; the theoretical yield, based on Fe, is 14.25 g.

PROPERTIES:

Formula weight 159.1. Insoluble in water; indefinitely stable in dry air.

REFERENCES:

K. Preis. J. prakt. Chem. 107, 12 (1869); R. Schneider. Ibid. 108, 16 (1869).

Basic Iron (III) Sulfate

$Fe_2(SO_4)_3(OH)_6 \cdot 2\,H_2O$ or $3\,Fe_2O_3 \cdot 4\,SO_3 \cdot 9\,H_2O$

$$3\,Fe_2(SO_4)_3 + 14\,H_2O = 2\,Fe_2(SO_4)_3(OH)_6 \cdot 2\,H_2O + 5\,H_2SO_4$$
$$\text{1/10:} \quad 120.0 \quad 25.2 \quad 96.1 \quad 49.0$$

The basic sulfate, which is stable over a large temperature range (up to 170°C), is readily obtained in crystalline form by

heating a sealed tube containing an approximately 20% solution of $Fe_2(SO_4)_3$ at 150°C. The product is a fine, orange-yellow powder consisting of small, transparent, cubelike rhombohedra.

REFERENCES:

E. Posniak and H. E. Merwin, J. Amer. Chem. Soc. 44, 1965 (1922); N. V. Shishkin, Zh. Obshch. Khim. 21, 456 (1951); Athanasesco. Comptes Rendus Hebd. Seances Acad. Sci. 103, 271 (1886).

Basic Iron (III) Acetate

$$[Fe_3(CH_3COO)_6(OH)_2]CH_3COO \cdot H_2O$$

$$\underset{320.6}{3\,Fe(OH)_3} + \underset{420.2}{7\,CH_3COOH} = \underset{632.7}{[Fe_3(CH_3COO)_6(OH)_2]CH_3COO \cdot H_2O} + 6\,H_2O$$

The monoacetate of the complex base, which occurs predominantly in the monoacidic form, crystallizes readily from dilute acetic acid (about 10% or 1.6 N). The triacetate is formed only from solutions containing at least 65% acetic acid by weight (11.4 N); these are allowed to stand in a vacuum desiccator over conc. H_2SO_4.

To prepare the monoacetate, a very dilute $FeCl_3$ solution is treated at room temperature with aqueous NH_3; the precipitate is washed for several days with cold water, which is frequently decanted, and washed thoroughly again on a filter. The slurry of hydrated iron oxide thus obtained is dissolved (heating) in about an equal amount of acetic acid. Crystallization takes place if the solution is allowed to stand in an open dish for several days in a well-ventilated spot. After filtration, the salt is kept for some time over soda lime to absorb the acetic acid.

SYNONYM:

Triiron (III) hexaacetatodihydroxomonoacetate.

PROPERTIES:

Transparent, brick-red rhombic leaflets. Dissolves slowly in cold water, rapidly in hot water. Only sparingly soluble in acetic acid.

REFERENCES:

A. Krause, Z. anorg. allg. Chem. 169, 286 (1928); R. Weinland and E. Gussmann, Ber. dtsch. chem. Ges. 42, 3888 (1909); Z. anorg. Chem. 66, 157 (1910).

Hexacyanoferric (II) Acid

$$H_4Fe(CN)_6$$

$$\underset{422.4}{K_4Fe(CN)_6 \cdot 3H_2O} + \underset{145.9}{4HCl} + \underset{148.2}{2(C_2H_5)_2O} = \underset{364.1}{H_4Fe(CN)_6 \cdot 2(C_2H_5)_2O} + \underset{298.2}{4KCl} + 3H_2O$$

A solution of 42 g. of $K_4Fe(CN)_6 \cdot 3H_2O$ in 350 ml. of water is mixed with 100 ml. of conc. HCl (d 1.19); any KCl which separates is redissolved by addition of some water. After thorough chilling, about 50 ml. of ether is added. The etherate separates in several hours as colorless tablets. These are filtered off, washed with a small quantity of dilute HCl containing some ether, and redissolved in 50 g. of alcohol. After residual undissolved KCl is removed by filtration, the compound is reprecipitated by addition of 50 g. of ether, filtered off, and washed with ether. It is finally transferred to a round flask and converted to $H_4Fe(CN)_6$ by heating at 40–50°C in aspirator vacuum.

SYNONYMS:

Hydrogen hexacyanoferrate (II), ferrocyanic acid.

DropBooks

PROPERTIES:

Snow-white when pure. d (25°) 1.536. Indefinitely stable if dry; gradually becomes blue in moist air. Elimination of HCN begins at about 100°. Readily soluble in water or alcohol; insoluble in ether or acetone. The bright lemon-yellow aqueous solution decomposes on heating or in light. Solubility (14°) 13 g./100 g. of aqueous solution.

REFERENCES:

W. Biltz, Z. anorg. allg. Chem. 170, 161 (1928); A. Mittasch and E. Kuss, Z. Elektrochem. 34, 159 (1928).

Ammonium Hexacyanoferrate (II)

$$(NH_4)_4Fe(CN)_6$$

$$\underset{216.0}{H_4Fe(CN)_6} + \underset{68.1}{4NH_3} = \underset{284.1}{(NH_4)_4Fe(CN)_6}$$

To prepare a completely potassium-free salt, a conc. aqueous solution of pure hexacyanoferric (II) acid is neutralized with pure

10% aqueous NH_3; the salt which precipitates is collected, washed several times with alcohol and then with ether.

PROPERTIES:

Readily soluble in water, insoluble in alcohol. In vacuum, decomposition begins above 100°C.

REFERENCE:

A. Mittasch and E. Kuss, Z. Elektrochem. 34, 59 (1928).

Hexacyanoferric (III) Acid

$H_3Fe(CN)_6$

$$\underset{329.3}{K_3Fe(CN)_6} + \underset{109.4}{3\,HCl} = \underset{214.9}{H_3Fe(CN)_6} + \underset{223.7}{3\,KCl}$$

Cold saturated $K_3Fe(CN)_6$ solution (40 ml.) is treated slowly and in the cold with 40 ml. of fuming HCl; the mixture is allowed to stand in an ice bath with frequent agitation for about half an hour. The KCl precipitate is removed by filtration and the filtrate is shaken with 70 ml. of ether. Three layers are formed: aqueous, oily and ethereal. After draining the aqueous layer, the middle, oily layer is allowed to clarify. It is then separated from the ether layer and the oil is completely freed of ether under vacuum. This results in crystallization of a yellow etherate of $H_3Fe(CN)_6$; finally, however, pure $H_3Fe(CN)_6$ remains as a brown mass. The acid may be recrystallized by solution in absolute ethanol and evaporation of the solvent. The compound must not be allowed to contact metal or rubber and should be kept as dry as possible.

SYNONYM:

Hydrogen hexacyanoferrate (III), ferricyanic acid.

PROPERTIES:

Rather readily soluble in water and alcohol; unlike $H_4Fe(CN)_6$, it is also soluble in ether-alcohol mixtures. The aqueous solution is yellow to brown.

REFERENCE:

W. M. Cumming and D. G. Brown, J. Soc. Chem. Ind. Trans. 44, 110 (1925).

Sodium Hexathiocyanoferrate (III)

$$Na_3Fe(SCN)_6 \cdot 12\,H_2O$$

$$\underset{106.9}{Fe(OH)_3} + \underset{177.2}{3\,HSCN} + \underset{243.2}{3\,NaSCN} + 9\,H_2O = \underset{689.4}{Na_3Fe(SCN)_6 \cdot 12\,H_2O}$$

Aqueous HSCN solution is added in the cold to a known amount of freshly precipitated and well washed hydrated iron (III) oxide until the solid is barely dissolved. Then NaSCN is added until about nine moles of NaSCN are present for each mole of $Fe(SCN)_3$. The solution is allowed to stand in a desiccator over conc. H_2SO_4 for several weeks; very dark-red crystals, which exhibit an intense green color when viewed by reflected light, separate out. On further evaporation of the mother liquor, precipitation of NaSCN also begins; on heating, the Fe^{3+} is partly reduced.

SYNONYM:

Sodium iron (III) thiocyanate.

PROPERTIES:

Deliquescent in air; converted to the trihydrate by storage over conc. H_2SO_4. Soluble in alcohol, giving a permanganate-like violet color; may be recrystallized from such solutions without decomposition.

DropBooks

REFERENCES:

G. Krüss and H. Moraht. Liebigs Ann. 260, 209 (1890); A. Rosenheim and R. Cohn. Z. anorg. Chem. 27, 295 (1901); H. I. Schlesinger and H. B. van Valkenburgh. J. Amer. Chem. Soc. 53, 1215 (1931).

Sodium Pentacyanoamminoferrate (II)

$$Na_3[Fe(CN)_5NH_3] \cdot 3\,H_2O$$

$$\underset{298.0}{Na_2[Fe(CN)_5NO] \cdot 2\,H_2O} + \underset{34.1}{2\,NH_3} + \underset{40.0}{NaOH}$$

$$= \underset{326.0}{Na_3[Fe(CN)_5NH_3] \cdot 3\,H_2O} + N_2 + H_2O$$

A mixture of 30 g. of $Na_2[Fe(CN)_5NO] \cdot 2\,H_2O$ with 120 ml. of water is prepared and cooled in an ice-salt mixture. Ammonia is then introduced at +10°C until saturation; the temperature during

this operation must not exceed 20°C. The solution is allowed to remain under a loose cover for several hours (not longer) at 0°C, and the crystals which separate from the deep brownish-yellow solution are collected by filtration. The remainder of the compound can be precipitated from the solution by addition of CH_3OH. The product may be purified by solution in some cold water, from which it is precipitated as fine, bright-yellow needles by careful addition of 90% alcohol.

The hexahydrate is hygroscopic and readily loses NH_3. It is dried to constant weight by storing for several days in a vacuum desiccator over $CaCl_2$. It then contains three (or, according to Hölzl, 2.5) moles of H_2O. Yield: 24 g. (73%). The yellow aqueous solution decomposes on heating, precipitating the hydroxide.

REFERENCES:

K. A. Hofmann, Z. anorg. Chem. 10, 264 (1895); W. Manchot, E. Merry and P. Woringer, Ber. dtsch. chem. Ges 45, 2876 (1912); F. Hölzl and K. Rokitansky, Monatsh. Chem. 56, 82 (1930).

Sodium Pentacyanoamminoferrate (III)

$$Na_2[Fe(CN)_5NH_3] \cdot H_2O$$

$$\underset{328.0}{Na_3[Fe(CN)_5NH_3] \cdot 3\,H_2O} + \underset{69.0}{NaNO_2} + \underset{60.0}{CH_3COOH} =$$

$$\underset{266.9}{Na_2[Fe(CN)_5NH_3] \cdot H_2O} + \underset{30.0}{NO} + \underset{40.0}{NaOH} + \underset{82.0}{CH_3COONa} + 2\,H_2O$$

A solution of 20 g. of $NaNO_2$ in 50 ml. of water is treated at 0°C with 20 ml. of 30% acetic acid and then with 30 g. of $Na_3[Fe(CN)_5NH_3] \cdot 3\,H_2O$. After two hours, 1:1 alcohol-ether is added; this first precipitates a violet aquo complex salt (formed in a side reaction); further addition of the alcohol-ether mixture precipitates the desired salt. This is purified by repeated solution in cold water and reprecipitation with alcohol. The dark-yellow powder is dried to constant weight in vacuum over conc. H_2SO_4; it then contains one or two moles of water.

The salt dissolves readily in water, giving a brownish-red color.

REFERENCES:

K. A. Hofmann, Liebigs Ann. 312, 24 (1900); F. Hölzl and K. Rokitansky, Monatsh. Chem. 56, 82 (1930).

SECTION 28

Cobalt, Nickel

O. GLEMSER

Metallic Cobalt

I. Prepared by reduction of precipitated cobalt oxalate with hydrogen.

Cobalt oxalate, precipitated in the cold, is dried at 120°C and ground to a fine powder. It is then reduced with H_2 (six hours at 500°C), with the temperature being raised rapidly at the beginning of the run. The product is cooled, ground and reduced once more; the fine metal powder is stored in a glass vessel under alcohol.

DropBooks

II. VERY PURE COBALT

Impurities, principally Fe, Cu and Ni, are removed by various precipitation reactions and by electrolysis. Finally, very pure Co is deposited electrolytically from a $CoSO_4$ solution. According to Kershner, Hoertel and Stahl, the pure metal still contains 0.001–0.002% Ni, 0.001–0.003% Fe, a maximum of 0.001% Cu, and 0.005% S.

A) REMOVAL OF IMPURITIES

A solution of the cobalt (II) salt is treated with $Na_2CO_3 \cdot 10\,H_2O$, added in small portions and with stirring, until the pH reaches 3.5; then 1 N Na_2CO_3 solution is added until the cobalt carbonate just barely precipitates. The precipitated carbonates are removed by filtration. Following this, 8 ml. of a saturated aqueous solution of 1,2-cyclohexanedione dioxime is added for each 10 mg. of Ni, Cu and Fe present in the filtrate. The Ni precipitates out; the suspension is heated for one hour at 90–95°C with occasional stirring, and the precipitate is filtered off.

The solution, which should now contain about 10% Co, is adjusted to a pH of 5.5 with H_2SO_4 or Na_2CO_3. Then, 0.2 moles of pyridine is added per liter of solution; the latter is electrolyzed

at 25°C (stirring), using a mercury cathode (206 cm.^{2} of surface area) and a platinum sheet anode. The cathode potential stays constant at 0.78 volt. At a Ni content of 0.05–0.10 g./liter of solution, the electrolysis requires eight hours; at a level of 0.5 g. of Ni/liter, it takes 24–32 hours.

After the electrolysis, the solution is filtered and the $Co(OH)_2$ precipitated from the filtrate by addition of NaOH. The precipitate is washed by decantation with hot distilled water until the odor of pyridine is no longer apparent. The precipitate is then filtered off and dissolved in dilute H_2SO_4 in such a way as to give a solution containing 90–100 g. of Co. This solution then constitutes the starting material for the electrolytic separation of the metal (see the following).

B) SEPARATION OF THE METAL.

The electrolysis cell is a 4-liter beaker with a side arm through which the solution can overflow into a collecting vessel. To avoid contamination from external sources, the cell and collecting vessel are placed in a glass cabinet. The solution is passed through the cell at 1–2 liters per hour, the pH being maintained at 1.2–1.6 by addition of the pyridine-free $CoSO_4$ solution. The electrolysis conditions are: 50–55°C, three platinum anodes and two titanium cathodes (the latter having about the same surface area as the anodes), cathode current density 40 amp./in.^{2} The deposit of highly purified cobalt can be removed from the titanium cathodes.

To avoid accumulation of impurities in the electrolyte, the latter is periodically (as the need arises) reprocessed according to the procedure given in subsection A on removal of impurities (filtration, precipitation, washing and redissolution in H_2SO_4).

Alternate method: Reduction of CoO or Co_3O_4 with H_2 for five hours at 500°C (Gmelin, 8th ed., volume on cobalt).

PROPERTIES:

Atomic weight 58.94. Black metallic powder. M.p. 1492°C, b.p. 3183°C. Ferromagnetic. Readily soluble in dil. HNO_3; passivated by conc. HNO_3.

REFERENCES:

I. W. Biltz. Z. anorg. allg. Chem. 134, 25 (1924); G. F. Hüttig and R. Kassler. Z. anorg. allg. Chem. 187, 24 (1930).
II. K. K. Kershner, F. W. Hoertel and J. C. Stahl. U. S. Dept. Interior, Bur. Mines Rep. Invest. 1956, I (Chem. Zentr. 1957, 255).

Cobalt (II) Chloride

$CoCl_2$

I. $\underset{(6H_2O)}{CoCl_2 \cdot 6H_2O} + 6\,SOCl_2 = CoCl_2 + 12\,HCl + 6\,SO_2$

238.0 713.9 129.9 437.6 384.4

Fine $CoCl_2 \cdot 6H_2O$ powder is placed in a flask provided with a ground joint and is covered with $SOCl_2$. The mixture is refluxed for several hours. The excess $SOCl_2$ is then evaporated on a steam bath. The $SOCl_2$ which clings to the product is removed by repeated evacuation of the flask.

II. $\underset{249.1}{Co(CH_3COO)_2 \cdot 4H_2O} + \underset{471.0}{6\,CH_3COCl} =$

$CoCl_2 + 2(CH_3CO)_2O + 4\,CH_3COOH + 4\,HCl$

129.9 204.2 240.2 145.9

A Pyrex tube 18 × 200 mm. is charged with 4.0 g. of fine $Co(CH_3COO)_2 \cdot 4H_2O$ powder. It is then closed off with a rubber stopper; the latter carries a dropping funnel and a fritted-glass filtering finger. Then, 15 ml. of benzene is added with agitation (magnetic stirrer), followed by CH_3COCl (slow addition until about 10% excess). The mixture is stirred for 30 minutes, the $CoCl_2$ precipitate allowed to settle, and the mother liquor siphoned off through the filtering finger. The residue is treated with benzene and CH_3COCl to complete the reaction. The supernatant liquid is removed by filtration and the $CoCl_2$ is washed three or four times with anhydrous benzene; it is then dried for two hours at 150°C under nitrogen.

Alternate methods: a) Heating of $CoCl_2 \cdot 6H_2O$ with $COCl_2$ in a sealed tube at 200°C [H. Hecht (1947)].

b) Heating of $CoCl_2 \cdot 6H_2O$ in a stream of dry HCl at 160–170°C [G. L. Clark, A. J. Quick and W. D. Harkins, J. Amer. Chem. Soc. 42, 2483 (1920)]. Simple heating at 140°C yields a somewhat basic salt.

PROPERTIES:

Leaflets, colorless in very thin layers, pale blue in layers over 1 mm. thick. M.p. 735°C, b.p. 1049°C; d_4^{25} 3.367. Heat of formation (25°C): —77.8 kcal./mole. Decomposes on long heating in air at 400°C. Sublimes at 500°C in HCl gas, forming loose crystalline fragments. Hygroscopic. Solubility in H_2O (g. of $CoCl_2$/100 g. of solution): 29.5 (0°C); 34.86 (20°C); 51.93 (98°C). Soluble in

methanol, ethanol, acetone, pyridine and ether. Crystal structure: C19 type.

REFERENCES:

I. H. Hecht. Z. anorg. Chem. 254, 51 (1947).
II. G. W. Watt, P. S. Gentile and E. P. Helvenston. J. Amer. Chem. Soc. 77, 2752 (1955).

Hexaamminecobalt (II) Chloride

$[Co(NH_3)_6]Cl_2$

$$\underset{(6H_2O)\ 238.0}{CoCl_2} + 6\,NH_3 = \underset{232.0}{[Co(NH_3)_6]Cl_2}$$

NH_3: 102.2

A mixture of 15 g. of $CoCl_2 \cdot 6\,H_2O$ and 14 ml. of H_2O is heated to boiling in the absence of air and treated hot with sufficient conc. NH_3 to produce complete solution; the solution is then filtered. Deaerated alcohol (air boiled out under reflux) is added to the hot filtrate until a permanent clouding is just barely obtained. The solution is cooled in running water and the solid thus precipitated is filtered off. It is washed with 1:1 conc. NH_3: alcohol, then with the same mixture in 1:2 ratio, and lastly with deaerated, NH_3-saturated alcohol. The product is dried over KOH in a high vacuum. Yield: 7 g.

The precipitation, washing, filtration and drying must be carried out in an O_2-free atmosphere (for technique see Part I).

Alternate method: Passage of NH_3 over $CoCl_2$ at room temperature [W. Biltz and B. Fetkenheuer (1914)].

PROPERTIES:

Flesh-colored powder or rose-red crystals. In high vacuum over H_2SO_4 (65-67°C), converts to blue *trans*-$[CoCl_2(NH_3)_2]$. Relatively stable to O_2 when dry; gradually oxidized in air when moist. Readily soluble in dil. ammonia, sparingly soluble in conc. ammonia, insoluble in alcohol. d_4^{25} 1.479. Crystal structure: Jl_1 (K_2PtCl_6) type.

REFERENCE:

W. Biltz and B. Fetkenheuer. Z. anorg. allg. Chem. 89, 97 (1914).

Cobalt (II) Bromide

$CoBr_2$, $CoBr_2 \cdot 6H_2O$

ANHYDROUS $CoBr_2$

I. $$\underset{326.9}{CoBr_2 \cdot 6H_2O} = \underset{218.8}{CoBr_2} + \underset{108.1}{6H_2O}$$

Prepared by careful heating of $CoBr_2 \cdot 6H_2O$ to 130–150°C, followed by sublimation in high vacuum at 500°C.

II. Treatment of $Co(CH_3COO)_2 \cdot 4H_2O$ with CH_3COBr in benzene in a manner analogous to the preparation of $CoCl_2$.

Alternate methods: *a*) Heating of $CoBr_2 \cdot 6H_2O$ in a stream of HBr at 500°C [G. Crut, Bull. Soc. Chim. France [4] 35, 550 (1924)].

b) Allowing $CoBr_2 \cdot 6H_2O$ to stand for one week over conc. H_2SO_4 [G. L. Clark and H. K. Bruckner (1922)].

PROPERTIES:

Green solid or lustrous green crystalline leaflets. M.p. 678° (under HBr and N_2); d_4^{25} 4.909. Heat of formation: −63.8 kcal./mole. Hygroscopic; in air, transforms to $CoBr_2 \cdot 6H_2O$. Readily soluble in H_2O (red color). Saturated aqueous solution contains 66.7 g. of $CoBr_2$ at 59°C, 68.1 g. at 97°C (per 100 g. solution). Readily soluble in methanol, ethanol, acetone and methyl acetate; sparingly soluble in tetranitromethane. Crystal structure: C 6 type.

REFERENCES:

G. L. Clark and H. K. Bruckner. J. Amer. Chem. Soc. 44, 230 (1922); W. Biltz and E. Birk. Z. anorg. allg. Chem. 127, 34 (1923); G. W. Watt, P. S. Gentile and E. P. Helveston. J. Amer. Chem. Soc. 77, 2752 (1955).

$CoBr_2 \cdot 6H_2O$

Precipitated cobalt carbonate is dissolved in aqueous HBr (d 1.49). The solution is heated on the steam bath until a deep blue color appears; it is then concentrated by evaporation on the steam bath. Cooling in ice water precipitates crystals of the hexahydrate; these are filtered off and washed with ice water.

PROPERTIES:

Formula weight 326.88. Red crystals. M.p. 47–48°C; d_4^{25} 2.46. Deliquescent in air. All water is removed by standing over conc. H_2SO_4 or by heating to 130–140°C.

REFERENCE:

G. L. Clark and H. K. Bruckner. J. Amer. Chem. Soc. 44, 230 (1922).

Cobalt (II) iodide

α-CoI_2, β-CoI_2, $CoI_2 \cdot 6\,H_2O$

α-CoI_2

$$Co + 2\,HI = CoI_2 + H_2$$
$$58.9 \quad 255.8 \quad 312.8 \quad 22.4\,l.$$

Fine Co powder obtained from cobalt oxalate is heated to 400–500°C in a stream of HI (4–5 hours). The product iodide is melted by heating to 550°C and allowed to cool in high vacuum.

PROPERTIES:

Black, graphitelike solid. M.p. 515–520°C (in high vacuum); d_4^{25} 5.584. Heat of formation: −39.13 kcal./mole. Solubility in H_2O: 58.7% (−2°C); 66.4% (25°C); 80.9% (111°C). Dilute solutions are red; concentrated solutions are red at low temperatures, while at higher temperatures all shades from brown to olive green are present. Very hygroscopic, becomes blackish green in air. Soluble in $SOCl_2$, $POCl_3$. Crystal structure: C 6 type.

REFERENCE:

W. Biltz and E. Birk. Z. anorg. allg. Chem. 127, 34 (1923).

β-CoI_2

Sublimation of α-CoI_2 in high vacuum yields β-CoI_2.

The starting α-CoI_2 is placed at location a of the tube shown in Fig. 333 and heated slowly in a high vacuum to 570–575°C. Cobalt metal remains as a residue at a, and a black sublimate of α-CoI_2 is deposited at b. Ochre-yellow β-CoI_2 appears at c, as do the I_2 crystals present in the tube. The tube is placed in a horizontal furnace in such a way that the section from a to d is at 100°C. The section projecting from the furnace is fanned with a flame until all I_2 collects at e. The loosely adhering β-CoI_2 is shaken from c into f. The apparatus is filled with N_2, and f with its contents is sealed off. About 0.8 g. of β-CoI_2 is obtained from 10 g. of α-CoI_2.

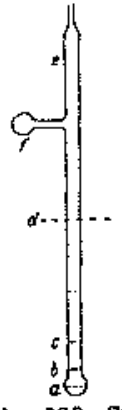

Fig. 333. Sublimation of cobalt(II) iodide.

PROPERTIES:

Ochre-yellow powder. d_4^{25} 5.45. Very hygroscopic; deliquesces in moist air, forming green droplets. Solution in H_2O is colorless, becoming rose-colored on heating. Blackens at 400°C and converts to α-CoI_2.

REFERENCE:

E. Birk and W. Biltz. Z. anorg. allg. Chem. 128, 46 (1923).

$CoI_2 \cdot 6\,H_2O$

Precipitated cobalt carbonate or $Co(OH)_2$ is dissolved in aqueous HI. The solution is concentrated on a steam bath to a sirupy consistency and is then allowed to cool. The product is filtered off and washed with some water.

Alternate method: A solution of CoI_2 in water is cooled to a low temperature [G. L. Clark and H. K. Bruckner, J. Amer. Chem. Soc. 44, 230 (1922)].

PROPERTIES:

Formula weight 420.86. d 2.90. Long, dark-red crystals, which begin to lose water of crystallization above 27°C and become anhydrous at 130°C.

DropBooks

REFERENCES:

O. Erdmann. J. prakt. Chem [1] 7, 254 (1836); A. Étard. Ann. Chim. Phys. [7] 2, 503 (1894).

Cobalt (II) Oxide

CoO

Prepared by thermal decomposition of cobalt salts containing a volatile acid moiety.

Cobalt carbonate, precipitated from $Co(NO_3)_2 \cdot 6\,H_2O$ with aqueous Na_2CO_3 in the absence of air, is heated for several hours in high vacuum at 350°C.

Analysis for active oxygen is necessary (treatment with hydrochloric acid and determination by the Bunsen method).

Alternate method: (The product is less certain to have the composition CoO): heating of $Co(NO_3)_2 \cdot 6\,H_2O$ or CoC_2O_4 to 1000°C and cooling in a stream of N_2.

PROPERTIES:

Formula weight 74.94. d_4^{18} 6.47. Heat of formation: —57.5 kcal./mole. Olive-green powder; takes up O_2 from air at room temperature. Becomes brown, and finally black, as the oxygen content increases. Stable in air when calcined at a high temperature. Converts to Co_3O_4 on heating in air at 390–900°C. Readily soluble in HCl, H_2SO_4 and HNO_3. Fine CoO powder is also soluble in conc. alkali. Crystal structure: B1 (NaCl) type.

REFERENCE:

M. Le Blanc and E. Moebius, Z. phys. Chem. (A) 142, 151 (1929).

Cobalt (II,III) Oxide

Co_3O_4

Precipitated cobalt carbonate is heated for one hour at 700°C. Analysis for active oxygen is required (treatment with hydrochloric acid and determination by the Bunsen method).

Alternate methods: a) Heating of $Co(NO_3)_2 \cdot 6H_2O$ at 700°C (crucible, one hour) (J. A. Hedvall and T. Nilson).

b) Heating of CoO in air at 700°C [L. Wöhler and O. Balz, Z. Elektrochem. 27, 406 (1921)].

PROPERTIES:

Formula weight 240.82. d 6.073. Heat of formation: —206.1 kcal./mole. Blackish-gray powder. Converts in air to CoO (905–925°C). Coarse crystalline Co_3O_4 is attacked only by conc. H_2SO_4; fine powder dissolves slowly in acids. Crystal structure: H 11 (spinel) type.

REFERENCE:

J. A. Hedvall and T. Nilson, Z. anorg. allg. Chem. 205, 425 (1932).

Cobalt (III) Hydroxide

CoO(OH)

$$\underset{(6H_2O)}{Co(NO_3)_2} + 3\,KOH + \tfrac{1}{2}Br_2 = CoO(OH) + 2\,KNO_3 + KBr + H_2O$$

291.1 168.3 79.9 91.9 202.2 119.0

A solution of 56 g. of KOH in 300 ml. of H_2O is added dropwise (stirring) to a solution of 90 g. of $Co(NO_3)_2 \cdot 6H_2O$ and 12 ml. of

Br_2 in 1300 ml. of H_2O. The resulting precipitate settles in about three hours. It is washed by decantation with four 5-liter portions of CO_2-free water. Should the precipitate undergo peptization on repeated addition of wash water, it is filtered on a Zsigmondy membrane filter, suction-dried and slurried in five liters of CO_2-free water. The slurry is filtered as above and the solid dried in a vacuum desiccator over conc. H_2SO_4.

All operations (precipitation, decantation and filtration) must be conducted in a CO_2-free atmosphere. After drying in the vacuum desiccator, this precaution is no longer necessary.

Alternate methods: *a*) Air oxidation of a solution of $CoCl_2 \cdot 6H_2O$ in aqueous NaOH [W. Feitknecht and W. Bédert, Helv. Chim. Acta 24, 683 (1941)].

b) Precipitation of $[Co(NH_3)_6]Cl_3$ with aqueous KOH [G. F. Hüttig and R. Kassler (1929)].

ANALYSES REQUIRED:

Co (electrolytic), H_2O, CO_2, and active oxygen (treatment with hydrochloric acid and determination by the Bunsen method).

Used as an oxidation catalyst.

PROPERTIES:

Black powder. d 4.29–4.90. Converts to Co_3O_4 on heating in vacuum at 148–150°C. Dissolves in HCl, evolving Cl_2. Soluble in HNO_3 and H_2SO_4. Not attacked by aqueous alkali or ammonia. Solution in organic acids such as oxalic or tartaric, accompanied by reduction.

DropBooks

REFERENCE:

G. F. Hüttig and R. Kassler, Z. anorg. allg. Chem. 184, 279 (1929).

Cobalt (II) Hydroxide

$Co(OH)_2$

$$\underset{(6\,H_2O)\ 291.1}{Co(NO_3)_2} + \underset{112.2}{2\,KOH} = \underset{93.0}{Co(OH)_2} + \underset{202.2}{2\,KNO_3}$$

ROSE-COLORED $Co(OH)_2$

A solution of 40 g. of $Co(NO_3)_2 \cdot 6H_2O$ in 1000 g. of H_2O, cooled to 0°C, is added dropwise and with vigorous shaking to a solution of 40 g. of KOH in 500 g. of H_2O maintained at 0°C. The

initial blue color of the precipitate rapidly turns to rose. The precipitate is washed by decantation with CO_2- and O_2-free water until K^+ and NO_3^- ions can no longer be detected. It is then filtered off and dried in a desiccator over 50% H_2SO_4.

Precipitation, washing, filtration and drying must be carried out in an atmosphere free of CO_2 and O_2, since $Co(OH)_2$ oxidizes very readily (for technique, see Part I).

ANALYSES REQUIRED:

Co (electrolytic) H_2O and CO_2.

PROPERTIES:

Rose-red powder. d_4^{18} 3.597. Heat of formation: — 63.4 kcal. per mole. Converts to CoO + H_2O when heated in vacuum at 168°. Oxidation leads to higher cobalt hydroxides. Readily soluble in acids, insoluble in dil. alkalies, appreciably soluble in ammonia. Crystal structure: C 6 type.

REFERENCE:

G. F. Hüttig and R. Kassler. Z. anorg. allg. Chem. 187, 16 (1930).

BLUE $Co(OH)_2$

A small excess of NaOH solution is added to a 0.1 M cobalt salt solution containing about 1% glucose. The precipitate is thoroughly washed in the absence of air with aqueous alcohol, aqueous acetone and finally with pure acetone. It is then dried. The resulting blue hydroxide changes color very readily on drying (oxidation).

When only small quantities are needed, 5 ml. of the 0°C, 0.1 M cobalt salt solution is treated with 5.2 ml. of 0°C, carbonate-free 0.2 N NaOH in a small Erlenmeyer flask. The precipitate and the mother liquor are poured at once into a centrifuge tube chilled in ice-salt mixture and frozen. The tube, containing the frozen block of solution plus precipitate, is then removed from the ice-salt bath; as soon as the block detaches from the glass tube it is crushed in a porcelain mortar and melted in the centrifuge tube by addition of 25% alcohol. The precipitate is rapidly centrifuged and washed twice with chilled aqueous acetone and with pure acetone. The acetone clinging to the blue precipitate is evaporated in vacuum.

PROPERTIES:

Blue powder. Constitution: "double-layer lattice," related to C 6 type.

REFERENCE:

W. Feitknecht. Helv. Chim. Acta 21, 766 (1938) and private communication.

Cobalt Sulfides

CoS, CoS_2, Co_3S_4, Co_9S_8

α-CoS

$$\underset{(6H_2O)}{Co(NO_3)_2} + H_2S = CoS + 2HNO_3$$
$$\underset{291.1}{} \qquad \underset{22.4\ l.}{} \qquad \underset{91.0}{} \qquad \underset{126.0}{}$$

Precipitated in the same way as α-NiS. The product is dried for 90 hours, with the temperature raised slowly from 100 to 540°C. The sulfide dried at 300°C is pyrophoric.

Catalyst for pressure hydrogenation of organic compounds.

PROPERTIES:

Black powder, soluble in HCl. Forms Co(OH)S in air. Amorphous (by x-ray analysis). Heat of formation: −21.71 kcal./mole.

DropBooks

REFERENCE:

E. Dönges. Z. anorg. Chem. 253, 346 (1947).

β-CoS

$$\underset{58.9}{Co} + \underset{32.1}{S} = \underset{91.0}{CoS}$$

Fine Co powder is mixed with the stoichiometric quantity of fine S powder and heated at 650°C for 2–3 days in an evacuated, sealed quartz tube. The tube is then quenched in cold water.

Analyses for Co and S are necessary. The compound is used as catalyst in the hydrogenation of organic compounds.

Alternate method: A 1 N solution of $CoCl_2$ is treated with acetic acid and precipitated with H_2S; workup is the same as in the case of α-CoS.

PROPERTIES:

Gray powder. M.p. 1135°C; d 5.45. Soluble in acids. Crystal structure: B8 type. Long heating at 200°C produces a modification with a complicated structure. Material with an overall formula $CoS_{1.0}$ is not homogeneous; the CoS phase has the composition $CoS_{1.04}$–$CoS_{1.13}$.

REFERENCES:

D. Lundquist and A. Westgren. Z. anorg. allg. Chem. 239, 85 (1938); E. Dönges. Z. anorg. Chem. 253, 346 (1947).

CoS_2

I.

Co	+ 2S	→	CoS_2
58.9	64.1		123.1

Stoichiometric quantities of Co and S powders are mixed and reacted in the same way as described in the case of β-CoS.

II. REACTION OF H_2S WITH COBALT (III) COMPLEXES

Dry, H_2-free H_2S is allowed to react with $[Co(NH_3)_5Cl]Cl_2$ or $[Co(NH_3)_6]Cl_3$. The temperature is raised to 600–630°C over a period of one hour, and maintained at this level for two hours. The product is allowed to cool to 200°C in the stream of H_2S; then the H_2S is displaced with dry CO_2 and the product is cooled further. It is sensitive to air; it is heated with S in a sealed tube (one day at 750°C), and the excess S is extracted with CS_2 after the reaction is complete.

Analyses for Co and S are required. Used as a catalyst in organic syntheses.

PROPERTIES:

Gray-black crystalline powder; d 4.269. Liberates S when heated in absence of air. Not attacked by nonoxidizing acids or alkalies. Crystal structure: C 2 type.

REFERENCES:

I. D. Lundquist and A. Westgren. Z. anorg. allg. Chem. 239, 85 (1938).
II. O. Hülsmann and W. Biltz. Ibid. 224, 73 (1935).

Co_3S_4 (H11 type) and Co_9S_8 (cubic crystalline) are prepared in the same way as β-CoS: heating stoichiometric quantities of Co and S powders in an evacuated, sealed quartz tube at 650°C. [D. Lundquist and A. Westgren (1938)].

Cobalt (III) Sulfate

$Co_2(SO_4)_3 \cdot 18\,H_2O$

A sulfuric acid solution of $CoSO_4 \cdot 7\,H_2O$ (formula wt. 281.11) is anodically oxidized at 0°C.

A porous clay cell (about 120 ml. capacity) is charged with a solution of 24 g. of $CoSO_4 \cdot 7H_2O$ in 75 ml. of warm 8 N H_2SO_4. A cylindrical Pt sheet (4 cm. high, 12 cm. wide), which serves as anode, is also inserted. A Pt wire welded to the sheet serves as the electrical lead. A Cu cylinder (8 cm. high) with a suitable electrical lead is placed around the clay cell and serves as the cathode. The cathode electrolyte is 8 N H_2SO_4. The electrolysis vessel is cooled in ice water. The electrolysis starts when the anode electrolyte has reached 30°C and takes about 12 hours. The thick, deep-blue suspension is rapidly filtered through a fritted-glass funnel and is then pressed dry on a clay plate with a Pt spatula.

Alternate method: Gaseous fluorine is passed through an ice-cold solution of 24 g. of $CoSO_4 \cdot 7H_2O$ in 150 ml. of 8 N H_2SO_4 [F. Fichter and H. Wolfmann, Helv. Chim. Acta 9, 1093 (1926)].

PROPERTIES:

Formula weight 730.37. Lustrous, blue-green leaflets. Decomposes rapidly in ice-cold water, liberating O_2 and yielding $CoSO_4$. Dilute H_2SO_4 gives a green solution which is stable for several days. Aqueous NaOH precipitates CoO(OH). Decomposes rapidly when heated in dry air, forming a brown (later reddish) powder. Powerful oxidizing agent.

DropBooks

REFERENCE:

E. Muller. Elektrochem. Praktikum [Laboratory Manual for Electrochemistry], 5th ed., Leipzig, 1940, p. 218.

Cobalt Aluminate

$CoAl_2O_4$

$$\underset{74.9}{CoO} + \underset{102.0}{Al_2O_3} = \underset{176.9}{CoAl_2O_4}$$

A stoichiometric mixture of CoO and Al_2O_3 is prepared and then mixed with 1.5 times its weight of KCl. The mixture is heated to about 1100°C in a porcelain crucible. The melt is cooled, pulverized, and extracted with boiling water until no further Cl- reaction is obtained. The residue is dried at 60°C in a drying oven.

SYNONYM:

Thenard's blue.

PROPERTIES:

M.p. 1700-1800°; d_4^{18} 4.37. Not attacked by Cl_2, mineral acids or aqueous alkalies. Decomposed by fusion with $KHSO_4$ and by heating with H_2SO_4 in a sealed tube at 200°C. Crystal structure: H11 (spinel) type.

REFERENCES:

J. A. Hedvall. Z. anorg. allg. Chem. 92, 305 (1915); 96, 72 (1916).

Hexaamminecobalt (III) Nitrate

$[Co(NH_3)_6](NO_3)_3$

$$\underset{267.5}{[Co(NH_3)_6]Cl_3} + \underset{189.0}{3\,HNO_3} = \underset{347.2}{[Co(NH_3)_6](NO_3)_3} + \underset{109.4}{3\,HCl}$$

A solution of $[Co(NH_3)_6]Cl_3$ in a minimum quantity of water is prepared and dil. HNO_3 is added; the resulting precipitate is washed with dil. HNO_3 until free of the chloride ion, then with 90% alcohol until free of acid.

PROPERTIES:

Yellow tetragonal prisms. d_4^{25} 1.804. Solubility in H_2O in moles/liter: 0.0202 (0°C); 0.052 (20°C); 0.0704 (30°C).

REFERENCE:

S. M. Jörgensen. Z. anorg. Chem. 17, 457 (1898).

Cobalt (III) Amide

$Co(NH_2)_3$

Fluffy $Co(NH_2)_3$ precipitates upon addition of KNH_2 to a solution of $[Co(NH_3)_6](NO_3)_3$ in liquid NH_3.

$$\underset{347.2}{[Co(NH_3)_6](NO_3)_3} + \underset{165.4}{3\,KNH_2} = \underset{107.0}{Co(NH_2)_3} + \underset{102.2}{6\,NH_3} + \underset{303.3}{3\,KNO_3}$$

The process requires a supply of N_2 entirely free of oxygen traces (see p. 458 ff.); this nitrogen is then passed through a wash bottle with conc. KOH, a drying tower with solid KOH, and two U tubes with P_2O_5. The stream of N_2 is then led to a manifold,

from which it may be directed through stopcocks to various reaction vessels and auxiliary apparatus such as transfer and storage tubes. A branch terminating in a mercury-filled beaker serves as a pressure-relief valve.

In addition, a stream of very pure NH_3 is required; this may be taken from a storage cylinder which contains some Na metal. The NH_3 is passed through a drying tube containing $NaNH_2$ and then a fritted-glass disk (not too fine) to remove any entrained solid particles. The NH_3 line has two side branches, one terminating in a vent stopcock, the other in an Hg manometer. The NH_3 line must be capable of withstanding pressures to about 10 atm.; thus, it must contain no ground joints and only a few well-secured stopcocks. The NH_3 line itself terminates in the above-mentioned manifold.

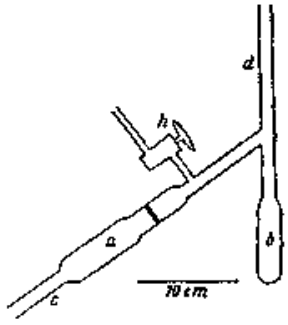

Fig. 334. Pressure vessel for preparation of cobalt (III) amide. Stopcock *h* and associated tubing are perpendicular to the plane of the diagram. The plug in *h* is held in place by a clamp to prevent it from being blown out by pressure in the apparatus.

The reaction takes place in the pressure-resistant vessel shown in Fig. 334. This vessel and accessory equipment are attached to the manifold via flexible couplings made of lead tubing or corrugated pinchbeck (copper-zinc alloy); thus, they may be connected to the N_2 or NH_3 streams, as desired, and also can be moved to some extent.

The pressure apparatus is first heated while the N_2 stream passes through. Then, 1.5–2 g. of $[Co(NH_3)_6](NO_3)_3$ is admitted through *a* from a charging funnel and placed on the fritted-glass disk. The tube is then sealed at *c*. Next, a few mg. of Pt black and the required quantity of metallic K (3 moles of K per mole of $[Co(NH_3)_6](NO_3)_3$ + 5% excess K) are placed in reactor *b*, and the tube is sealed at *d*. The stopcock on the N_2 line is closed and the valve on the NH_3 cylinder is opened. When the manometer in the NH_3 line shows about 4 atm., the valve is closed and the NH_3 is vented to the atmosphere by opening the vent stopcock. This purging process is repeated three times to displace the N_2 from the apparatus. Then reactor *b* is immersed in ice-salt mixture, the valve on the NH_3 cylinder fully opened, and NH_3 allowed to condense in *b* until the latter is 3/4 full of liquid. Stopcock *h* is then closed and tube *a* is cooled so that NH_3 distills from *b* into *a*. The hydrogen evolved in the reaction of K with NH_3 is vented

from time to time by carefully opening *h* and the vent stopcock in the NH_3 line. All of the potassium is allowed to react, whereby all the $[Co(NH_3)_6](NO_3)_3$ dissolves. The apparatus is then tilted while tube *a* is cooled. The KNH_2 solution is thereby filtered into *a* (at the same time, the apparatus is rocked to mix the contents). Reactor *b* is then recooled, thus recondensing the NH_3 in it; this liquid NH_3 is again filtered into *a*. This procedure is repeated three times in order to react all of the KNH_2. The reaction mixture is allowed to remain in *a* for six hours (ice cooling and frequent shaking). It is then filtered into *b*, the precipitate being retained on the fritted-glass disk. The ammonia is again evaporated from *b* and condensed in *a*, shaken there with the solid, and filtered into *b* once more. This is repeated ten times, after which the precipitate is completely free of KNO_3. Finally, the NH_3 is vented by opening *h* as well as the vent stopcock in the NH_3 line. Nitrogen is then introduced into the apparatus, which is then inverted and opened by breaking the seal at *c*. The amide on the filter plate is crushed with the aid of a bent Ni spatula, and transferred (in a stream of N_2) through the open end of *a* into a storage device (see Part I, Fig. 54b for the latter). This storage tube is also purged with very pure N_2 and, after the amide has been introduced, is closed with a ground stopper. The storage tube is cooled in ice while N_2 is passed over the amide until no further NH_3 is given off.

ANALYSIS:

The product amide is placed in a small glass bulb (air must be excluded). The bulb is then sealed. The following may then be done:

Determination of NH_3: Aqueous KOH is added to the amide and the liberated NH_3 is distilled into a known quantity of acid.

Determination of Co: The $Co(OH)_3$ which precipitates on addition of KOH is dissolved in sulfurous acid and the Co determined by analytical electrolysis.

The NO_3^- is determined with diphenylamine.

PROPERTIES:

Chocolate-brown powder; sometimes pyrophoric. Soluble in dil. acids with brown-red color, and in cold water with brown color; the slightly cloudy liquid gradually deposits brownish-black cobalt (III) hydroxide. Forms CoN in vacuum at 40–50°C. Heating in liquid NH_3 produces CoN, Co_3N and $CoN_{0.29}$.

REFERENCE:

O. Schmitz-Dumont, J. Pilzecker and H. F. Piepenbrinck. Z. anorg. allg. Chem. 248, 175 (1941).

Dicobalt Nitride

Co_3N

$$2\,Co + NH_3 = Co_3N + 1^1/_2\,H_2$$
$$117.9 \quad 22.4\,l. \quad 131.9 \quad 33.7\,l.$$

Ten mg. of Co_3O_4 is reduced with pure H_2 by heating in a corundum boat for two hours at 350°C. The resulting Co powder is then heated for three hours at 380°C in a stream of NH_3 which passes through the tube at 22 cm./sec. The product is ground and treated once more under the same conditions.

The reduction and nitridation must be carried out in one continuous operation, since the Co powder obtained by reduction of Co_3O_4 is pyrophoric. The cobalt powder prepared from cobalt oxalate cannot be completely converted to nitride under these conditions.

Alternate method: Thermal degradation of $Co(NH_2)_3$ in vacuum at 160°C [O. Schmitz-Dumont, Angew. Chem. 67, 231 (1955); J. Clarke and K. H. Jack, Chem. and Ind. 1951, 1004].

PROPERTIES:

Grayish-black powder. d 6.4. In the cold, dil. acids and alkalies react slowly, conc. HCl rapidly, and conc. HNO_3 violently. Warm dil. acids also dissolve Co_3N rapidly. The slow attack by acids gives a quantitative yield of the NH_4 salts (this is an analytical method), while vigorous decomposition evolves part of the nitrogen as N_2. Forms a nitride with the approximate composition Co_3N on thermal decomposition. In vacuum, stable until formation of the compound $CoN_{0.41}$ at 200°C; at 250°C, hexagonal metallic Co containing small amounts of Ni is produced. Crystal structure: rhombically deformed hexagonal close packing of metal atoms.

REFERENCE:

R. Juza and W. Sachse, Z. anorg. Chem. 253, 45 (1945).

Cobalt Nitride

CoN

$$Co(NH_2)_3 = CoN + 2\,NH_3$$
$$107.0 \quad 72.9 \quad 44.8\,l.$$

Cobalt amide is placed in a vapor-pressure eudiometer (see Part I, Fig. 85) and carefully decomposed at 50–70°C in the absence

of air. The NH_3 evolved is absorbed in conc. H_2SO_4. The degradation is continued until all NH_3 has been eliminated. The CoN thus formed is transferred in the absence of air to a glass bulb, which is then sealed off. The exact stoichiometric composition is never attained, since a small amount of N_2 is evolved along with the NH_3. The degration products usually have the composition $CoN_{0.8}$-$CoN_{0.9}$.

ANALYSIS:

To determine the valence of Co, the sample is carefully heated with 2 N KOH until NH_3 can no longer be detected. The resulting blue liquid, which contains suspended cobalt (*III*) hydroxide, is treated with KI and $NaHCO_3$ in a flask closed off with a glass stopper, and is then carefully acidified. After standing for one day, the I_2 which separates is back-titrated with $Na_2S_2O_3$ solution.

PROPERTIES:

Black powder; pyrophoric. The nitrogen content of the degradation product drops off with increasing degradation temperature (the composition $CoN_{0.5}$, corresponding to the formula Co_2N, is obtained at 160°C). Heating in the presence of H_2O and aqueous alkali liberates NH_3. Dilute H_2SO_4 liberates part of the bound nitrogen as N_2. Crystal structure: B 1 type.

REFERENCES:

O. Schmitz-Dumont, H Broja and H. F. Piepenbrink, Z. anorg. Chem. 253, 118 (1947); O. Schmitz-Dumont, Angew. Chem. 67, 231 (1955).

Cobalt Phosphides

CoP_3, CoP, Co_2P

Prepared by heating stoichiometric quantities of pure Co metal and red P for 20 hours at 650-700°C in sealed, evacuated quartz tubes. The starting Co powder is obtained by reduction of CoO or Co_3O_4 with H_2 at 700°C.

Co	+ 3 P	= CoP_3;	Co	+ P	= CoP;	2 Co	+ P	= Co_2P
58.9	92.9	151.9	58.9	31.0	89.9	117.9	31.0	148.9

PROPERTIES:

CoP_3: Grayish-black powder; d_4^{25} 4.26.

CoP: Grayish-black powder; d_4^{25} 6.24. Crystal structure: B 21 type.

Co_2P: Grayish-black powder; d_4^{25} 7.4. Crystal structure: C 23 type.

REFERENCES:

CoP_3: W. Biltz and M. Heimbrecht. Z. anorg. allg. Chem. 241, 349 (1939).
CoP: K. E. Fylking. Ark. Kem. Mineral. Geol. 11 (B), No. 48 (1934).
Co_2P: H. Nowotny. Z. anorg. Chem. 254, 31 (1947).

Dicobalt Carbide

Co_2C

$$\underset{117.9}{2\,Co} + \underset{44.8\,l.}{2\,CO} = \underset{129.9}{Co_2C} + \underset{22.3\,l.}{CO_2}$$

Fine Co powder, obtained from CoO and H_2 at 280–300°C, is heated at 220°C with dry, O_2-free CO (flow rate 0.75 liter/hour) for 550 hours. Reduction of the oxide and preparation of the carbide must be carried out in one continuous operation, since the Co powder is pyrophoric. The temperature must be held exactly at 220°C since Co_2C decomposes above 225°C.

ANALYSIS:

Heating of Co_2C (9.24% C) with H_2 at 250°C gives a quantitative yield of CH_4 (free C gives no CH_4 under these conditions).

DropBooks

PROPERTIES:

Metallic-gray powder. Decomposes between 260 and 310°C. Hydrogen converts the orthorhombic carbide to a hexagonal form between 198 and 275°C, N_2 between 297 and 369°C, and CO_2 between 364 and 540°C. Space group of the rhombic carbide: d_{2h}^{14}.

REFERENCES:

H. A. Bahr and V. Jessen. Ber. dtsch. chem. Ges. 63, 2226 (1930); J. E. Hofer and W. C. Beebles. J. Amer. Chem. Soc. 69, 893 (1947).

Hexaamminecobalt (III) Chloride

$[Co(NH_3)_6]Cl_3$

$$\underset{(6H_2O)\ 951.8}{4\,CoCl_2} + \underset{214.0}{4\,NH_4Cl} + \underset{340.6}{20\,NH_3} + \underset{22.4\,l.}{O_2} = \underset{1070.0}{4\,[Co(NH_3)_6]Cl_3} + \underset{36.0}{2\,H_2O}$$

A mixture of 240 g. of $CoCl_2 \cdot 6\,H_2O$, 160 g. of NH_4Cl, and 200 ml. of H_2O is shaken until solution is almost complete. Then 4–5 g.

of activated charcoal and 500 ml. of conc. ammonia are added, and a fast stream of air is passed through the mixture until the red solution becomes yellow-brown. The air flow should not be so rapid as to reduce the ammonia content; should this occur, some additional conc. ammonia may be added.

The precipitated $[Co(NH_3)_6]Cl_3$ and the charcoal are filtered off, and the residue is dissolved in hot 1-2% HCl. The solution is filtered hot and the pure product is precipitated by adding 400 ml. of conc. HCl and chilling to 0°C. The precipitate is collected, washed first with 60% alcohol, then with 95% alcohol, and finally dried at 80-100°C. Yield: 85%.

Alternate method: From $[Co(NH_3)_5Cl]Cl_2$ and ammonia [S. M. Jörgensen, Z. anorg. Chem. 17, 455 (1898)].

SYNONYM:

Luteocobalt chloride.

PROPERTIES:

Wine-red or brownish-red monoclinic crystals. d_4^{25} 1.710. Solubility in H_2O in moles/liter: 0.152 (0°C); 0.26 (20°C); 0.42 (46.6°C); Boiling in water yields $Co(OH)_3$.

REFERENCES:

J. Bjerrum. Metal Ammine Formation in Aqueous Solution, p. 241, Copenhagen, 1941; J. Bjerrum and J. P. McReynolds in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 217.

Chloropentaamminecobalt (III) Chloride

$[Co(NH_3)_5Cl]Cl_2$

Obtained by oxidation of an ammoniacal $CoCl_2$ solution, and purified via $[Co(NH_3)_5H_2O]_2(C_2O_4)_3 \cdot 4H_2O$.

A) CRUDE PRODUCT, $[Co(NH_3)_5Cl]Cl_2$

A solution of 20 g. of precipitated cobalt carbonate in some 1:1 HCl is prepared, filtered and cooled; a mixture of 250 ml. of conc. ammonia and 50 g. of $(NH_4)_2CO_3$ dissolved in 250 ml. of H_2O is then added. The mixture is oxidized for three hours by bubbling in a stream of air. After addition of 150 g. of NH_4Cl the solution is evaporated to sirup consistency on the steam bath. Dilute HCl is added to drive off the CO_2 and produce a weakly acid reaction;

then ammonia is added to give a weakly basic solution, followed by 10 ml. of additional conc. ammonia. The liquid, whose volume at this point is 400–500 ml., is heated on the steam bath until all the tetraammine salt disappears; it is then treated with 300 ml. of conc. HCl and heated for 30–45 minutes on the steam bath. The $[Co(NH_3)_5Cl]Cl_2$ precipitates on cooling. It is filtered off and washed with 1:1 HCl until free of NH_4Cl, then with alcohol until free of acid. The salt still contains some $[Co(NH_3)_6]Cl_3$. Yield: 34.5 g.

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 5, 361 (1894).

B) AQUOPENTAAMMINECOBALT (III) OXALATE, $[Co(NH_3)_5(H_2O)]_2(C_2O_4)_3 \cdot 4H_2O$

A mixture of 10 g. of finely powdered crude $[Co(NH_3)_5Cl]Cl_2$, 75 ml. of H_2O, and 50 ml. of 10% ammonia is heated on the steam bath in an Erlenmeyer flask covered with a watch glass (continuous agitation) until all of the basic aquopentaammine chloride dissolves and a deep-red solution forms. The solution is filtered, the filtrate is made very weakly acid with oxalic acid, and some additional $(NH_4)_2C_2O_4$ is added to complete the precipitation. The slurry is allowed to stand; the precipitate is then filtered off and washed with cold water. The yield of the dry salt is about 12 g.

DropBooks

SYNONYM:

Roseocobalt oxalate.

PROPERTIES:

Formula weight 660.36. Brick-red crystals. Solubility in water at 17.5°C is 0.0019 moles/liter.

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 19, 78 (1899).

C) PURE CHLOROPENTAAMMINECOBALT (III) CHLORIDE, $[Co(NH_3)_5Cl]Cl_2$

Twenty grams of $[Co(NH_3)_5(H_2O)]_2(C_2O_4)_3 \cdot 4H_2O$ is dissolved in 150 ml. of 2% ammonia in the cold, and the insoluble $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ (luteooxalate) is filtered off. The filtrate is precipitated in the cold with dil. HCl. The $[Co(NH_3)_5Cl]Cl_2$ thus formed is filtered off, washed successively with alcohol, absolute alcohol and ether, and dried in air.

The purification method given by Jörgensen does not yield completely pure $[Co(NH_3)_5Cl]Cl_2$.

ANALYSIS:

Ionizable Cl and total Cl are determined in order to determine whether impurities are present.

SYNONYM:

Chloropurpureocobalt chloride.

PROPERTIES:

Formula weight 250.47. Ruby-red crystals. d_4^{25} 1.783. Solubility in H_2O: 0.0089 (0°C); 0.0225 (25°C); 0.040 (50°C) moles/liter. The presence of HCl lowers the solubility; at 25°, 10% HCl dissolves 0.00067 moles/liter. Neutral aqueous solutions decompose when boiled, and $Co(OH)_3$ is deposited. Heating to higher temperatures produces $CoCl_2$. Crystal type: orthorhombic-bipyramidal.

REFERENCE:

F. J. Garrick. Z. anorg. allg. Chem. 224, 27 (1935).

Nitropentaamminecobalt (III) Chloride

$[Co(NH_3)_5NO_2]Cl_2$

$$[Co(NH_3)_5Cl]Cl_2 + NaNO_2 = [Co(NH_3)_5NO_2]Cl_2 + NaCl$$
$$250.5 \qquad 69.0 \qquad 261.0 \qquad 58.4$$

A mixture of 20 g. of $[Co(NH_3)_5Cl]Cl_2$, 200 ml. of H_2O, and 50 ml. of 10% ammonia is placed in an Erlenmeyer flask covered with a watch glass, and heated on the steam bath until the salt dissolves (frequent shaking is necessary). The solution is filtered, the filtrate cooled and made weakly acidic with dil. HCl, 25 g. of crystalline $NaNO_2$ is added, and heating on the steam bath is continued until the initial red precipitate dissolves completely. The cold, brownish-yellow solution contains a copious deposit of crystals. At this point, 250 ml. of conc. HCl is added (carefully at first). After chilling, the product is filtered off, washed with 1:1 HCl, then with alcohol until free of acid, and dried in air. Yield: 17 g.

SYNONYM:

Xanthocobalt chloride.

PROPERTIES:

Brownish-yellow monoclinic crystals, d_4^{26} 1.804. Solubility in H_2O at 20°C: 0.11 moles/liter of solution; more soluble in hot H_2O. Decomposes on heating to 210°C.

REFERENCE:

S. M. Jörgensen. Z. anorg. Chem. 17, 463 (1898).

Nitritopentaamminecobalt (III) Chloride

$$[Co(NH_3)_5ONO]Cl_2$$

$$\underset{250.5}{[Co(NH_3)_5Cl]Cl_2} + \underset{69.0}{NaNO_2} = \underset{261.0}{[Co(NH_3)_5ONO]Cl_2} + \underset{58.4}{NaCl}$$

A solution of 10 g. of $[Co(NH_3)_5Cl]Cl_2$ in a mixture of 150 ml. of H_2O and 25 ml. of 10% ammonia is prepared with heating and agitation. The solution is filtered, cooled and exactly neutralized with dil. HCl. Then 25 g. of crystalline $NaNO_2$ is added and, when this has dissolved, 10 ml. of 1:1 HCl. The resulting precipitate is allowed to stand for several hours in the mother liquor while cooling in water; it is then filtered off and washed with cold water and alcohol.

DropBooks

PROPERTIES:

Chamois-colored crystalline powder, four times less soluble in water than nitropentaamminecobalt chloride. On standing for several weeks, converts to the isomeric form. The conversion is more rapid if a 10% aqueous solution of the compound is treated with an equal volume of conc. HCl.

REFERENCE:

S. M. Jörgensen. Z. anorg. Chem. 5, 168 (1894).

Carbonatotetraamminecobalt (III) Sulfate

$$[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$$

An aqueous solution of $CoSO_4$ is treated with $(NH_4)_2CO_3$ and NH_4OH, then oxidized in a stream of air.

Precipitated cobalt carbonate (20 g.) is dissolved in a minimum quantity of dil. H_2SO_4. The clear solution (about 100 ml.) is poured

into a solution of 100 g. of $(NH_4)_2CO_3$ in 500 ml. of H_2O and 250 ml. of conc. ammonia, and air is bubbled through for 2-3 hours. After complete oxidation, the blood-red solution, containing several small pieces of $(NH_4)_2CO_3$, is evaporated on a steam bath until the volume is 300 ml. The solution is then filtered, concentrated to 200 ml. and chilled, whereupon $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$ crystallizes as red prisms. The mother liquor is decanted; the precipitate is filtered off and washed once with a saturated solution prepared from a small portion of the precipitate. More salt is obtained by further evaporation of the mother liquor [add some $(NH_4)_2CO_3$]. Yield: 32 g.

PROPERTIES:

Formula weight 524.27. Garnet-red prisms, d 1.882. The aqueous solution decomposes on standing in light. Forms $[Co(NH_3)_4(H_2O)_2]SO_4$ (tetraammineroseocobalt sulfate) with dil. H_2SO_4. Loses all water over conc. H_2SO_4. Crystal form: orthorhomic-bipyramidal.

REFERENCE:

S. M. Jörgensen, Z. anorg. Chem. 2, 281 (1892).

Dichlorotetraamminecobalt (III) Chloride

$[Co(NH_3)_4Cl_2]Cl$

Two stable isomeric forms exist: these are the 1,2-dichloro- (*cis*-) and 1,6-dichloro- (*trans*-) compounds.

1,2-DICHLOROTETRAAMMINECOBALT (III) CHLORIDE (CIS), $[Co(NH_3)_4Cl_2]Cl \cdot 0.5H_2O$

Treatment of an ammoniacal solution of $Co(CH_3COO)_2 \cdot 4H_2O$ with $NaNO_2$, followed by air oxidation, affords $[Co(NH_3)_4(NO_2)_2]NO_2$, which is converted to the dichloro compound with conc. HCl.

Air is bubbled for five hours through a solution of 20 g. of $NaNO_2$ and 20 g. of $Co(CH_3COO)_2 \cdot 4H_2O$ in 200 ml. of 20% NH_3. The violet solution is concentrated to a small volume with occasional addition of solid $NaHCO_3$, then chilled. A large excess of alcohol is added to cause precipitation. The precipitate is filtered off, washed with alcohol-ether, and dried in a vacuum desiccator. This is *cis*-dinitrotetraamminecobalt (III) nitrite, which is not contaminated with the *trans* compound. It is very easily hydrolyzed.

The *cis*-nitrite is added in small portions to conc. HCl maintained at −10°C, giving a quantitative yield of the chloride.

SYNONYM:

Formerly: Chloroviolecobalt chloride.

PROPERTIES:

Formula weight 242.45. Violet needles. Water soluble; loses water of hydration at 60°C. Very unstable.

REFERENCE:

C. Duval. Comptes Rendus Hebd. Séances Acad. Sci. 182, 636 (1926).

DIAQUOTETRAAMMINECOBALT (III) SULFATE, $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$

This is formed by treatment of $[Co(NH_3)_4CO_3]_2(SO_4)_3 \cdot 3H_2O$ with dil. H_2SO_4.

A solution of 5 g. of pure $[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$ in 100 ml. of cold H_2O and 10 ml. of dil. H_2SO_4 is prepared; this results in evolution of CO_2. The clear solution is treated with 50–60 ml. of alcohol, added in small portions. The precipitate is filtered off, washed with 50% alcohol until free of acid, and dried in air. Yield: 6.2 g. (theoretical: 6.37 g.).

DropBooks

PROPERTIES:

Formula weight 668.45. Red quadratic prisms, which lose water of crystallization over conc. H_2SO_4. Solubility at 22°C: 0.175 moles/liter of water.

REFERENCE:

S. M. Jörgensen. Z. anorg. Chem. 2, 296 (1892).

1,6-DICHLOROTETRAAMMINECOBALT (III) CHLORIDE (TRANS), $[Co(NH_3)_4Cl_2]Cl \cdot H_2O$

A solution of 10 g. of $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$ in 50 ml. of cold conc. H_2SO_4 is prepared; the flask is allowed to stand for 24 hours, then placed in ice, and 50 ml. of conc. HCl is added dropwise with frequent and vigorous shaking. The *trans* salt separates in 48 hours. The flask is tilted and the mother liquor decanted as thoroughly as possible. Dilute HCl is then added; the precipitate is filtered off and washed with dil. HCl until free of H_2SO_4, then washed with alcohol until free of acid. Yield: 7.25 g. (theoretical: 7.53 g.).

SYNONYM:

Formerly: Chloropraseocobalt chloride.

PROPERTIES:

Formula weight 251.46. Lustrous green crystals. d^{25} 1.860. Loses water of crystallization in 1-2 hours at 100°C. Solubility at 0°: 0.0141 moles/liter H_2O; hydration in solution, yielding $[Co(NH_3)_4(H_2O)_2]Cl_3$. The *trans* compound is more stable than the *cis* form.

REFERENCE:

S. M. Jörgensen. Z. anorg. Chem. 14, 404 (1897).

Triethylenediaminecobalt (III) Bromide

$[Co\ en_3]Br_3$

The preparation from cobalt salt, ethylenediamine and NaBr yields the racemate of the optically active forms of $[Co\ en_3]Br_3$ as the first product. The racemate can be resolved with tartaric acid into the *d*- and *l*-tartrate, and further converted to the *d*- and *l*-bromide.

A) RACEMIC TRIETHYLENEDIAMINECOBALT (III) BROMIDE, $[Co\ en_3]Br_3 \cdot 3H_2O$

A solution of 10 g. of $CoCl_2 \cdot 6\ H_2O$ in 150 g. of 10% aqueous ethylenediamine is prepared and oxidized by bubbling air through it for several hours. The brown solution is then acidified with HCl and concentrated until crystallization. The crystal mass is dissolved in H_2O and treated with NH_4NO_3, which precipitates 1,6-$[Co\ en_2Cl_2]NO_3$. This precipitate is removed by filtration; then NaBr is added to the filtrate, whereupon completely pure $[Co\ en_3]Br_3 \cdot 3H_2O$ separates out.

PROPERTIES:

Formula weight 533.04. Small yellow needles. M.p. 271°; d_4^{25} 1.845. Solubility in H_2O at 16°C: 4.33 g. of anhydrous salt per 100 g. of solution.

B) RESOLUTION WITH TARTARIC ACID

A solution of 100 g. of $[Co\ en_3]Br_3$ in water is treated with the amount of silver tartrate (68.3 g.) needed for reaction with two atoms of bromine. After boiling, the AgBr precipitate is filtered off and then washed with boiling water until the water is no longer yellow. The filtrate and washings are combined and

concentrated. On chilling, the *d*-tartrate separates and is removed by filtration. The mother liquor is further concentrated and the additional precipitate of *d*-tartrate is removed. Cooling gels the solution to a mass of *l*-tartrate, still somewhat contaminated with *d*-tartrate.

C) *d*-TRIETHYLENEDIAMINECOBALT (III) BROMIDE TARTRATE
$[Co\ en_3]Br(d\text{-}C_4H_4O_6) \cdot 5H_2O$

The *d*-tartrate crystals obtained in B are recrystallized from hot water. Rapid cooling yields needles with a silky luster; these disappear on standing for 1–2 hours in the mother liquor and are replaced by coarse platelike crystals.

PROPERTIES:

Formula weight 557.32. Small bright-yellow needles or dark-yellow platelets. Optical rotation (1% solution) $[\alpha]_D$ +98°, $[M]_D$ +555°.

D) *d*-TRIETHYLENEDIAMINECOBALT (III) BROMIDE,
$d\text{-}[Co\ en_3]Br_3 \cdot 2H_2O$

The $d\text{-}[Co\ en_3]Br(C_4H_4O_6) \cdot 5H_2O$ obtained above is triturated with warm conc. HBr and the solution is filtered. On standing, large hexagonal tablets (acid bromide?) separate out; these are recrystallized from water to yield columnar crystals of the *d*-bromide.

PropBooks

PROPERTIES:

Formula weight 515.03. Yellow, columnar crystals. More readily soluble in H_2O than the racemic bromide. d_4^{25} 1.971. Optical rotation (1% solution): $[\alpha]_D$ + 117°; $[M]_D$ + 602°. Crystalline form: ditetragonal-bipyramidal.

E) *l*-TRIETHYLENEDIAMINECOBALT (III) BROMIDE,
$l\text{-}[Co\ en_3]Br_3 \cdot 2H_2O$

The gelatinous *l*-bromide tartrate is triturated with warm conc. HBr. The sparingly soluble racemic bromide tartrate which separates out is removed by filtration. On standing, the solution deposits crystals of *l*-bromide, which are recrystallized from hot water.

PROPERTIES:

Formula weight 515.03. Yellowish crystals. More readily soluble in H_2O than the racemic bromide. Optical rotation (1% solution): $[\alpha]_D$ −115°; $[M]_D$ −592°. Can be converted (with AgCl or $AgNO_3$) to the corresponding chloride or nitrate.

REFERENCE:

A-E: A. Werner. Ber. dtsch. chem. Ges. 45, 121 (1912).

Decaammine-μ-peroxocobalt (III) Cobalt (IV) Sulfate

$$[(NH_3)_5Co^{III}(O_2)Co^{IV}(NH_3)_5](SO_4)_2 \cdot SO_4H \cdot 3\,H_2O$$

The preparation involves oxidation of an ammoniacal solution of $CoSO_4 + (NH_4)_2SO_4$.

A mixture of 0.5 liter of 1 M $(NH_4)_2SO_4$, 1 liter of conc. ammonia, 1 liter of H_2O, 0.5 liter of 1 M $CoSO_4$, 0.5 liter of 1 M H_2O_2 and 0.5 liter of 1 M $(NH_4)_2S_2O_8$ is prepared in the indicated sequence, the solutions being added at approximately 10-second intervals. The mixture is vigorously agitated after each addition. After all additions have been completed it is allowed to stand for 10-15 minutes. Most of the supernatant liquid is siphoned off; the precipitate is filtered off, washed first with dil. ammonia and then with alcohol and suction-dried. The crude product (50-70 g.) is dissolved as rapidly as possible in 1250-1750 g. of 2 N H_2SO_4 (heating to 80-85°C is necessary). The solution is filtered at once and allowed to stand one day. The yield is 30-50 g. of pure product.

ANALYSIS:

$$2\,[Co_2(NH_3)_{10}O_2]^{4+} - 20\,H^+ + As^{3+} = 2\,O_2 + 4\,Co^{2+} + 20\,NH_4^+ + As^{5+}.$$

The product, in the sulfuric acid solution, is reduced with As^{3+}; the evolving O_2 is collected in an azotometer over strong KOH by means of CO_2. An aliquot of the solution is used to back-titrate the excess As^{3+} with $Ce(SO_4)_2$ and ferroin; another aliquot is used to determine Co by precipitation with 8-hydroxyquinoline and titration with $KBrO_3$.

PROPERTIES:

Formula weight 663.45. Grayish-black, lustrous prisms. Almost insoluble in cold dil. sulfuric acid; more soluble at 50-60°C.

REFERENCE:

K. Gleu and K. Rehm. Z. anorg. allg. Chem. 237, 79 (1938).

Sodium Hexanitritocobaltate (III)

$Na_3[Co(NO_2)_6]$

$$\underset{582.1}{2\,Co(NO_3)_2 \cdot 6\,H_2O} + \underset{828.0}{12\,NaNO_2} + \underset{120.1}{2\,CH_3COOH} + \underset{11.21.}{\tfrac{1}{2}\,O_2}$$

$$= \underset{340.0}{4\,NaNO_3} + \underset{164.1}{2\,CH_3COONa} + \underset{807.9}{2\,Na_3Co(NO_2)_6} + 7\,H_2O$$

A solution of 150 g. of $NaNO_2$ in 150 ml. of H_2O is cooled to 50–60°C; some of the $NaNO_2$ is thus reprecipitated. Then 50 g. of $Co(NO_3)_2 \cdot 6\,H_2O$ is added, followed by 50 ml. of 50% CH_3COOH in small portions (agitation). Then a fast stream of air is bubbled through for one half hour. After standing for two hours, the brown precipitate is filtered off. The filtrate must be clear at this point. The precipitate is stirred with 50 ml. of H_2O at 70–80°C. The solution is separated from undissolved $K_3[Co(NO_2)_6]$ on a small filter and combined with the above-mentioned clear filtrate. The combined solution (about 300 ml.) is treated with 250 ml. of 96% alcohol. The resulting precipitate is allowed to settle for about two hours, then filtered, suction-dried, washed four times with 25 ml. of alcohol, then twice with ether, and dried in air. Yield: 50–53 g. (75%).

Reprecipitation with alcohol is desirable. The pure preparation must give a perfectly clear solution in H_2O. To precipitate the salt, the alcohol is added from a wash bottle; during the addition, the flask is vigorously shaken to insure that the particle size of the precipitate will not be too small.

DoverBooks

SYNONYM:

Sodium cobaltinitrite.

PROPERTIES:

Yellow crystalline powder. Very soluble in water, sparingly soluble in alcohol and ether. The aqueous solution is not stable and forms HNO_2 and HNO_3. Crystal structure: $J2_1$ type (cubic).

REFERENCE:

E. Bijlman. Z. analyt. Chem. 39, 284 (1900).

Potassium Hexacyanocobaltate (III)

$K_3[Co(CN)_6]$

The intermediate $K_4[Co(CN)_6]$ is prepared from $Co(CN)_2$ and KCN. Boiling of its solution precipitates $K_3[Co(CN)_6]$.

A clear, filtered solution of 48 g. of $CoCl_2 \cdot 6\,H_2O$ in 500 ml. of H_2O is heated to boiling, and a clear solution of 30 g. of KCN

in 200 ml. of H_2O is added dropwise with vigorous stirring. Before adding the final portions of the KCN, a sample of the solution is filtered and the filtrate is treated with a drop of KCN solution, in order to establish whether any $CoCl_2$ is still present in the solution. The violet-red precipitate of $Co(CN)_2$ is filtered off, washed with cold H_2O, and dissolved while still moist in a conc. solution of 60 g. of KCN. The deep red solution of $K_4[Co(CN)_6]$ is heated to boiling for 10–15 min., whereupon it becomes yellow and evolves H_2. If a small quantity of yellow $K_3[Co(CN)_6]$ crystallizes at this time, some water is added to redissolve it. The boiling solution is filtered and cooled. The $K_3[Co(CN)_6]$ precipitate is collected on a filter and washed with some cold water. Further quantities of the precipitate are obtained by concentrating the mother liquor to half its volume; this solid is worked up as above. The combined precipitates are recrystallized twice from hot water, some activated carbon being added to the solution. The pure, almost colorless crystals are filtered off and washed with some cold water. They must give a clear water solution.

The small excess of KCN called for in the directions for preparing the solution of $Co(CN)_2$ in KCN prevents the precipitation of green $K_3Co[Co(CN)_6]$, which is insoluble at room temperature.

Alternate method: Oxidation of $CoCl_2 \cdot 6H_2O$ + KCN in acetic acid solution with air, and several reprecipitations from acetic acid solution with alcohol [W. Biltz, W. Eschweiler and A. Bodenstein, Z. anorg. allg. Chem. 170, 161 (1928)].

SYNONYM:

Potassium cobalt (III) hexacyanide.

PROPERTIES:

Formula weight 332.35. Small, almost colorless needles with a yellowish tinge. d_4^{25} 1.878. Readily soluble in water; solubility in 87–88% alcohol (20°C): 1:7500 parts. Decomposes on heating in absence of air. Crystalline form: monoclinic, isomorphic with $K_3Fe(CN)_6$.

REFERENCE:

A. Benedetti-Pichler, Z. anal. Chem. 70, 257 (1927).

Hexacyanocobaltic (III) Acid

$H_3Co(CN)_6$

$$\underset{332.4}{K_3Co(CN)_6} + \underset{109.4}{3\,HCl} = \underset{218.1}{H_3Co(CN)_6} + \underset{223.7}{3\,KCl}$$

A solution of 3 g. of $K_3Co(CN)_6$ in 9 ml. of H_2O is treated with 9 g. of conc. HCl. The KCl precipitate is removed by filtration.

The solution is sensitive to light.

SYNONYM:

Hydrogen hexacyanocobaltate (III).

REFERENCE:

A. von Baeyer and V. Villiger, Ber. dtsch. chem. Ges. 34, 2687 (1901).

$H_3Co(CN)_6 \cdot 5\,H_2O$

A very small excess of H_2SO_4 (d 1.84) is added to a 25% aqueous solution of $K_3Co(CN)_6$, which is then heated for 15–20 minutes to 50–55°C and cooled. Absolute alcohol is added and the alcohol-insoluble K_2SO_4 is removed by filtration. The solution is carefully concentrated at 50–55°C and the $H_3Co(CN)_6 \cdot 5\,H_2O$ thus formed is recrystallized three times from alcohol.

PROPERTIES:

Colorless crystalline needles; hygroscopic. Heating at 100°C yields white $H_3Co(CN)_6 \cdot 0.5\,H_2O$. At higher temperatures, colored products are formed until finally a black cobalt carbide remains. Not altered by brief boiling with HCl or HNO_3, but forms $Co_3[Co(CN)_6]_2$ in hot H_2SO_4 (d 1.84).

PrepBooks

REFERENCE:

O. K. Dobrolyubskiy, Zh. Prikl. Khimii 26, 1185, 1233 (1953).

Metallic Nickel

SABATIER METHOD

$$\underset{74.7}{NiO} + \underset{22.4\,l.}{H_2} = \underset{58.7}{Ni} + H_2O$$

Very pure, O_2-free H_2 dried over P_2O_5 is passed for 15 hours over NiO [obtained by thermal decomposition of $Ni(NO_3)_2 \cdot 6\,H_2O$] at 300–400°C. After cooling in the H_2 stream, the air-sensitive metal is transferred to small glass bulbs attached to the apparatus, and these are sealed off. The metal powder may also be stored in bottles under alcohol.

Used as hydrogenation catalyst.

PROPERTIES:

Atomic weight 58.71. Black metallic powder; pyrophoric. M. p. 1453°C, b.p. 3177°C. Ferromagnetic. Soluble in dil. HNO_3, passivated by conc. HNO_3.

REFERENCE:

P. Sabatier. Die Katalyse in der organischen Chemie [Catalysis in Organic Chemistry], translated into German and enlarged by B. Finkelstein and H. Häuber, Leipzig, 1927.

Nickel (II) Chloride

$NiCl_2$

I. $$\underset{\substack{(6\,H_2O)\\297.7}}{NiCl_2 \cdot 6\,H_2O} + \underset{713.9}{6\,SOCl_2} = \underset{129.6}{NiCl_2} + \underset{437.6}{12\,HCl} + \underset{384.4}{6\,SO_2}$$

Water is removed by refluxing with $SOCl_2$ as described for $CoCl_2$.

II. $$\underset{237.7}{NiCl_2 \cdot 6\,H_2O} = \underset{129.6}{NiCl_2} + \underset{108.1}{6\,H_2O}$$

The starting $NiCl_2 \cdot 6\,H_2O$ is dried in a combustion tube at 150°C; the final heating to 400°C proceeds in a stream of Cl_2-containing HCl. After the yellow $NiCl_2$ has formed, the tube is sealed at one end and the product is sublimed (oil-pump vacuum) at the highest temperature that the tube can withstand. To remove HCl, the $NiCl_2$ is annealed in high vacuum over KOH at 160°C.

Alternate methods: *a*) Heating of $NiCl_2 \cdot 6\,H_2O$ in a sealed tube with $COCl_2$ at 200°C (Hecht).

b) The frequently recommended thermal decomposition of $NiCl_2 \cdot 6\,NH_3$ does not yield pure $NiCl_2$, since black by-products are formed.

c) Treatment of $Ni(CH_3COO)_2 \cdot 4\,H_2O$ with CH_3COCl in benzene, analogous to the preparation of $CoCl_2$ [G. W. Watt, P. S. Gentile and E. P. Helvenston, J. Amer. Chem. Soc. 77, 2752 (1955)].

PROPERTIES:

Bright-yellow powder or crystalline leaflets (like mosaic gold). Subl. 993°C (760 mm.); m.p. 1001°C (in sealed tube); d_4^{25} 3.521. Heat of formation: −73.0 kcal./mole (25°C). Sublimed $NiCl_2$ is

relatively stable and takes up water slowly; fine $NiCl_2$ powder is hygroscopic and becomes green in air. Solubility in H_2O (g. $NiCl_2$/100 g. solution): 34.8 (0°C); 40.4 (26.3°C); 46.7 (100°C). Moderately soluble in methyl and ethyl alcohol. Crystal structure: C 19 type.

REFERENCES:

I. H. Hecht. Z. anorg. Chem. 254, 51 (1947).
II. W. Biltz and E. Birk. Z. anorg. allg. Chem. 127, 34 (1923).

Hexamminenickel (II) Chloride

$[Ni(NH_3)_6]Cl_2$

$$\underset{(6\,H_2O)}{NiCl_2} + 6\,NH_3 = [Ni(NH_3)_6]Cl_2$$
$$\underset{237.7}{} \qquad \underset{102.2}{} \qquad \underset{231.8}{}$$

A conc. solution of cobalt-free $NiCl_2 \cdot 6\,H_2O$ is treated with excess conc. NH_3, then cooled in running water. The separation of fine crystals of $[Ni(NH_3)_6]Cl_2$ is completed by addition of an ammoniacal NH_4Cl solution. The precipitate is filtered off and successively washed with conc. ammonia, alcohol and ether.

Alternate methods: Action of NH_3 on anhydrous $NiCl_2$ at room temperature [F. Ephraim, Z. phys. Chem. 81, 513 (1913)].

DropBooks

PROPERTIES:

Blue-violet, fine crystalline powder. d_4^{25} 1.468. Heat of formation: −16.3 kcal./mole. The decomposition pressure at 176.5°C is 1 atm. Decomposes in H_2O, liberating NH_3. Soluble in aqueous ammonia; not soluble in conc. ammonia or alcohol. Crystal structure: $J1_1$ type.

REFERENCE:

S. P. L. Sörensen. Z. anorg. Chem. 5, 354 (1894).

Nickel (II) Bromide

$NiBr_2$

ANHYDROUS $NiBr_2$

$$\underset{58.7}{Ni} + \underset{159.8}{Br_2} = \underset{218.5}{NiBr_2}$$

Nickel powder, produced by heating $NiCl_2$ in a hydrogen stream at 400°C, is covered with a layer of completely dry ether and then

treated with dry bromine. After 12 hours the ether is removed and the residue heated in vacuum at 130°C. In order to purify the preparation, which still contains some Ni, it is sublimed at 900°C (quartz or porcelain tube) in a CO_2-free stream of N_2 + HBr.

Alternate methods: *a)* Heating of $NiCl_2$ in a stream of HBr at 500°C (G. Crut).

b) Heating of $NiBr_2 \cdot 6H_2O$ at 140°C in a drying oven [J. A. A. Ketelaar, Z. Kristallog. 88, 26 (1934)].

c) Reaction of $Ni(CH_3COO)_2 \cdot 4H_2O$ with CH_3COBr in benzene, analogous to the preparation of $CoCl_2$ [G. W. Watt, P. S. Gentile and E. P. Helvenston, J. Amer. Chem. Soc. 77, 2752 (1955)].

PROPERTIES:

Yellow powder or bronze-yellow micalike particles. M. p. 963° (in sealed tube); d_4^{25} 5.018. Heat of formation: −51.8 kcal. per mole (25°). Solubility in H_2O (g. $NiBr_2$/100 g. solution): 56.6 (19°C); 61.0 (100°C). Soluble in methyl and ethyl alcohols, acetone and quinoline; insoluble in toluene. Crystal structure: sublimed product, C 19 type; unsublimed product, variable between C 6 and V 19 types.

REFERENCE:

G. Crut. Bull. Soc. Chim. France [4] 35, 550 (1924).

$NiBr_2 \cdot 6H_2O$

$$\underset{218.5}{NiBr_2} + \underset{108.1}{6H_2O} = \underset{326.6}{NiBr_2 \cdot 6H_2O}$$

A solution of $NiBr_2$ in water is concentrated until crystallization begins and is then cooled. The crystals are filtered off and recrystallized from alcohol.

Alternate method: Precipitated nickel carbonate or $Ni(OH)_2$ is dissolved in aqueous HBr, concentrated on the steam bath, and the product recrystallized from alcohol [J. A. A. Ketelaar, Z. Kristallog. 88, 26 (1934)].

PROPERTIES:

Green crystals; transform to $NiBr_2 \cdot 3H_2O$ at +28.5°C.

REFERENCE:

See G. L. Clark and H. K. Bruckner, J. Amer. Chem. Soc. 44, 230 (1922).

Nickel (II) Iodide

NiI_2

ANHYDROUS NiI_2

$$\underset{92.7}{Ni(OH)_2} + \underset{255.8}{2\,HI} = \underset{312.5}{NiI_2} + \underset{36.0}{2\,H_2O}$$

Either $Ni(OH)_2$ or precipitated nickel carbonate is dissolved in hydriodic acid and the solution evaporated to dryness. The solid is recrystallized from alcohol and dried at 140°C. A final sublimation in high vacuum at 500–600°C is recommended.

Alternate method: Dehydration of $NiI_2 \cdot 6\,H_2O$ (Riedel, Thesis, Univ. of Halle, 1913).

PROPERTIES:

Black solid; forms small lustrous crystals when sublimed. M.p. 797°C (in sealed tube); d_4^{25} 5.834. Heat of formation: —41.40 kcal./mole. Decomposes when heated to high temperatures in air. Hygroscopic; rapidly forms a green solution when exposed to air. Solubility in H_2O (g. NiI_2/100 g. solution): 57.8 (11°C); 64.1 (43°C); 65.7 (90°C). Aqueous solutions of NiI_2 can dissolve up to two atoms of iodine, thereby acquiring a brown color. Dilute solutions are pure green, concentrated solutions dirty green or reddish brown. Slowly soluble in cold absolute alcohol, rapidly in hot. Crystal structure: C 19 type.

REFERENCE:

J. A. A. Ketelaar. Z. Kristallogr. 88, 26 (1934).

$NiI_2 \cdot 6\,H_2O$

$$\underset{312.5}{NiI_2} + \underset{108.1}{6\,H_2O} = \underset{420.6}{NiI_2 \cdot 6\,H_2O}$$

A solution of NiI_2 in H_2O is evaporated to a sirup. The crystals of $NiI_2 \cdot 6\,H_2O$ are filtered off and suction-dried.

Alternate method: As in the case of NiI_2, but without the dehydration at 140°C [J. A. A. Ketelaar, Z. Kristallogr. 88, 26 (1934)].

PROPERTIES:

Blue-green crystals; rapidly deliquescent in air, becoming brown and giving off iodine. Exists up to 43°C; becomes anhydrous when heated on steam bath.

REFERENCES:

O. Erdmann. J. prakt. Chem [1] 7, 254(1936); A. Étard. Ann. Chim. Phys. [7] 2, 503 (1894).

Nickel (II) Oxide

NiO

Prepared by thermal decomposition of nickel salts of volatile acids.

I. Precipitated nickel carbonate or $Ni(NO_3)_2 \cdot 6H_2O$ is heated in a Pt crucible for six hours at 1000-1100°C and allowed to cool in O_2-free nitrogen.

On cooling in air, a surface skin forms, which can be removed by postreduction with pure H_2 at 100°C.

Test for active oxygen is essential.

II. Precipitated nickel carbonate is placed in a pear-shaped decomposition vessel, the air is displaced several times with O_2-free nitrogen, and the entire apparatus is degassed in high vacuum at 100°C. After high vacuum is established, the system is heated, over a period of 90 minutes, to 350°C. The product is transferred to previously prepared storage bulbs, which are then sealed.

The oxide blackens immediately in the presence of air. Test for active oxygen is essential.

Alternate method: Small chips of nickel are heated in air at 1000°C (for procedure, see method II, subsection on Cu_2O) [H. H. von Baumbach and C. Wagner, Z. phys. Chem. (B) 24, 61 (1934)].

Used as oxidation catalyst.

PROPERTIES:

Formula weight 74.71. M.p. 1990°C; d 6.67. Heat of formation: −58.4 kcal./mole. Bright-yellow powder, brown when heated. When the oxygen content is in slight excess, the color is dark olive green, becoming darker as the oxygen content increases. NiO prepared at high temperatures is almost insoluble in acids and alkalies; the lower the temperature of preparation, the more soluble it is, especially in hot nitric acid and ammonia. Crystal structure: B1 type.

REFERENCE:

M. Le Blanc and H. Sachse. Z. Elektrochem. 32, 58(1926).

Nickel (II) Hydroxide

$Ni(OH)_2$

$$\underset{(6\,H_2O)\ 290.8}{Ni(NO_3)_2} + 2\,NaOH = \underset{92.7}{Ni(OH)_2} + \underset{170.0}{2\,NaNO_3}$$
$$\qquad\qquad\qquad\quad 80.0$$

A solution of 25 g. of KOH in 250 ml. of carbonate-free H_2O is added dropwise and with vigorous stirring to a warm (about 35°C) solution of 60 g. of $Ni(NO_3)_2 \cdot 6\,H_2O$ in 250 ml. of H_2O. The precipitate is washed by decantation with several five-liter portions of warm, CO_2-free H_2O (until the washings are no longer alkaline), then once with five liters of CO_2-free H_2O containing some ammonia, and finally with similar portions of warm, CO_2-free water until both precipitate and washings are free of K^+ and NO_3^-. The precipitate is filtered off and dried in a vacuum desiccator over conc. H_2SO_4.

The preparation still contains about one mole of adsorptively bound water, which can be removed by heating to 200°C.

Precipitation, decantation and filtration are carried out in the absence of CO_2. Another suitable starting material is $Ni(NO_3)_2 \cdot 6\,NH_3$; however, $NiCl_2 \cdot 6\,H_2O$ and $NiSO_4 \cdot 7\,H_2O$ are not recommended, since the precipitate then tenaciously retains Cl^- and SO_4^{2-}.

DropBooks

PROPERTIES:

Apple-green crystalline powder; d 3.65. Decomposes at 230°C into NiO and H_2O. Soluble in ammonia, ethylenediamine and acids. Crystal structure: C 6 type. Heat of formation: −62.68 kcal./mole.

REFERENCE:

G. F. Hüttig and A. Peter, Z. anorg. allg. Chem. 189, 183 (1930).

β-Nickel (III) Hydroxide

NiO(OH)

$$\underset{(6\,H_2O)\ 290.8}{Ni(NO_3)_2} + \underset{166.3}{3\,KOH} + \underset{79.9}{{}^1/_2Br_2} = \underset{91.7}{NiO(OH)} + \underset{202.2}{2\,KNO_3} + \underset{119.0}{KBr} + \underset{18.0}{H_2O}$$

A solution of 100 g. of $Ni(NO_3)_2 \cdot 6\,H_2O$ in 1600 ml. of H_2O is added dropwise and with vigorous stirring to a solution of 55 g. of KOH and 12 ml. of Br_2 in 300 ml. of H_2O. The precipitation temperature should not exceed 25°C. The precipitate is washed

five times (decantation) with CO_2-free H_2O, then several times (decantation) using a centrifuge, until NO_3^- and K^+ can no longer be detected in either the precipitate or the wash water. The wet product is dried for three days over conc. H_2SO_4, then two weeks over 1:1 H_2SO_4.

Precipitation, decantation and filtration must be carried out in a CO_2-free atmosphere.

Tests for active oxygen, Ni, H_2O and CO_2 are necessary. The oxygen and H_2O contents vary. In view of the rapid conversion to $Ni_3O_2(OH)_4$, it is advisable to work up the precipitate as quickly as possible.

To determine active oxygen, a 100-mg. sample is covered with 100 ml. of H_2O, and 1 g. of KI and 25 ml. of 2 N H_2SO_4 are added. The liberated I_2 is titrated with $Na_2S_2O_3$.

Alternate method: A solution of $Ni(NO_3)_2 \cdot 6H_2O$ is treated with sodium acetate and electrolyzed at room temperature. The low yield is a disadvantage of this method [O. Glemser and J. Einerhand (1950)].

PROPERTIES:

Black powder, d_4^{20} 4.15. Readily soluble in acids. Rapidly converted to $Ni_3O_2(OH)_4$ by H_2O and bases. Loses water when heated in vacuum and is converted to $Ni_3O_2(OH)_4$. Crystal structure: C 6 type.

REFERENCES:

G. F. Hüttig and A. Peter. Z. anorg. allg. Chem. 189, 190 (1930); O. Glemser and J. Einerhand. Z. anorg. Chem. 261, 26 (1950).

γ-Nickel (III) Hydroxide

NiO(OH)

Metallic Ni is fused with Na_2O_2 + NaOH and the melt is extracted with H_2O.

A crucible of pure nickel is filled to one third of its volume with a mixture of one part of Na_2O_2 and three parts of NaOH, and heated for four hours at 600°C. The melt is cooled, then carefully extracted with ice water, avoiding any rise in temperature. Washing by decantation with H_2O is carried out until there no longer is an alkaline reaction. The tiny crystals settle very easily; the flocculent precipitate is removed by slurrying.

Tests for active oxygen [see under β-NiO(OH)], Ni, and H_2O are necessary.

Used as an oxidation catalyst.

PROPERTIES:

Small, lustrous, black hexagons or needles. d_4^{20} 3.85. Soluble in dil. H_2SO_4 with evolution of O_2. Decomposes on heating to 138–140°C. Crystal structure: resembles C 19 type.

REFERENCE:

O. Glemser and J. Einerhand. Z. anorg. Chem. 261, 26 (1950).

Nickel (II,III) Hydroxide

$Ni_3O_2(OH)_4$

The precipitation of $Ni_3O_2(OH)_4$ is carried out by dropwise addition of a solution of $Ni(NO_3)_2 \cdot 6H_2O$ to aqueous KOH + Br_2 at 50°C (as described under β-NiO(OH)). The product is washed by decantation with warm, CO_2-free H_2O. All operations are conducted in a CO_2-free atmosphere.

Tests for active oxygen: see under β-NiO(OH). Analysis for Ni and H_2O is recommended. Water and oxygen contents vary. Used as an oxidation catalyst.

Alternate method: Electrolysis (50–60°C) of a solution of $Ni(NO_3)_2$ treated with sodium acetate. The low yield is a disadvantage of this method (O. Glemser and J. Einerhand, see reference below).

DropBooks

PROPERTIES:

Formula weight 276.16. Black powder. d_4^{20} 3.33. Readily soluble in acids. On heating to 140°C, converts to NiO, H_2O and O_2. Crystalline form: hexagonal.

REFERENCES:

O. Glemser and J. Einerhand. Z. anorg. Chem. 261, 26 (1950).

Nickel (II) Sulfide

NiS

α-NiS

$$\underset{(6\,H_2O)\ 237.7}{NiCl_2} + H_2S = NiS + 2\,HCl$$

22.1 *l.* 90.8 72.9

The apparatus used for precipitation of nickel sulfides in the absence of air is shown in Fig. 335. The α-NiS is prepared

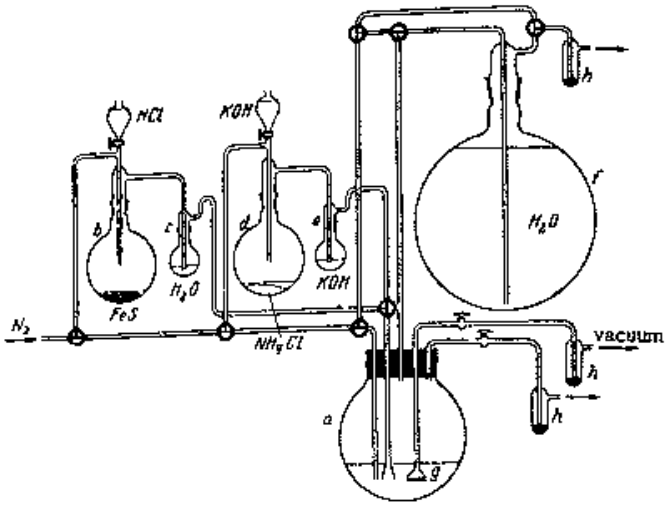

Fig. 335. Preparation of nickel sulfides in the absence of air.

as follows. The air is displaced from the apparatus by a stream of CO_2-free, O_2-free nitrogen. At the same time, all liquids in the apparatus are boiled and allowed to cool in the N_2 stream. These liquids comprise the solution in *a*, which is 0.4 N in $NiCl_2$ and 0.8 N in NH_4Cl; the water in *b*, which covers the chunks of FeS; the water in wash bottle *c*; the saturated NH_4Cl, with excess of solid NH_4Cl, in *d*; the conc. KOH in the bubble-counting tube *e*; and the wash water in *f*. The mercury trap *h* serves to prevent the entrance of air into the reactor. Now CO_2-free H_2S is generated in *b*, and the sulfide precipitates in *a*. The wash water is transferred into *a* (N_2 pressure), shaken with the precipitate, and (after the latter has settled) drawn off through fritted disc *g*, using a vacuum pump. The washing procedure is repeated 15-20 times.

The NiS should not be completely precipitated from the solution, otherwise it does not settle well during washing.

PROPERTIES:

Black powder, soluble in HCl. Converts to Ni(OH)S in air. Amorphous on x-ray analysis. Heat of formation: −19.37 kcal./mole.

REFERENCE:

E. Dönges, Z. anorg. Chem. 253, 345 (1947).

β-NiS

$$\underset{58.7}{Ni} + \underset{32.1}{S} = \underset{90.8}{NiS}$$

A stoichiometric mixture of Ni and S is heated for six hours at 900°C in a sealed, evacuated quartz tube.

Alternate methods: *a*) Precipitation with H_2S from a 1 N $NiCl_2$ solution containing acetic acid, workup as for α-NiS [A. Thiel and H. Gessner, Z. anorg. Chem. 86, 1 (1914)].

b) The alpha form of NiS is digested with 0.2 N acetic acid for several days in the absence of air (A. Thiel and H. Gessner, see above).

PROPERTIES:

Black powder. M.p. 810°; d 5.0–5.6. Dissolves rapidly on boiling in 2 N HCl. Crystal structure: B8 type.

REFERENCE:

W. Klemm and W. Schüth. Z. anorg. allg. Chem. 210, 39 (1933).

γ-NiS

$$\underset{(7\,H_2O)}{NiSO_4} + \underset{22.11.}{H_2S} = \underset{90.8}{NiS} + \underset{98.1}{H_2SO_4}$$
$$280.9$$

The apparatus shown for α-NiS is used and H_2S is bubbled through 1 N $NiSO_4$ solution weakly acidified with dil. H_2SO_4. Air must be rigorously excluded during the reaction. The precipitate is worked up in the same way as α-NiS.

PROPERTIES:

Black powder. d_4^{30} 5.34. Converts to β-NiS at 396°C. Crystal structure: B13 type.

REFERENCE:

R. G. Levi and A. Baroni. Z. Kristallogr. 92, 210 (1935).

DRYING OF PRECIPITATED NiS

The slurry of the sulfide is dried in a drying pistol for eight hours (aspirator vacuum); the temperature is slowly raised to 150°C. Then NaOH is placed in the drying pistol and the material is dehydrated for four additional hours at 180°C in an oil-pump vacuum.

DropBooks

The sulfide is then transferred to another small flask and dried for 5-12 hours at 300-400°C (high vacuum). The latter operation must be carried out with care, to avoid dusting of the product.

REFERENCES:

W. Biltz. Z. anorg. allg. Chem. 228, 275 (1936); 239, 82, 126 (1938).

Nickel (IV) Sulfide

NiS_2

$$\underset{90.8}{NiS} + \underset{32.1}{S} = \underset{122.8}{NiS_2}$$

Completely dry NiS is heated in a sealed tube with triple distilled S (five hours at 450°C). Four to five times the stoichiometric amount of S is used. After the reaction is complete, the excess S is removed by extraction with CS_2 in a Soxhlet apparatus.

Test for S: The sulfide is dissolved in HNO_3, and $BaCl_2$ is added to cause precipitation.

PROPERTIES:

Black to gray powder. d 4.39. Sensitive to air even when dry, evolving SO_2, which remains partly adsorbed. Can incorporate S into the crystal lattice. Soluble in nitric acid. Crystal structure: C2 type.

REFERENCES:

W. F. deJong and H. W. V. Willems. Z. anorg. allg. Chem. 160, 185 (1927); W. Biltz. Ibid. 228, 278 (1936).

Nickel (II) Amide

$Ni(NH_2)_2$

$$\underset{174.9}{Ni(SCN)_2} + 2\,\underset{110.2}{KNH_2} + \underset{80.8}{Ni(NH_2)_2} + 2\,\underset{194.4}{KSCN}$$

The apparatus shown in Fig. 334 [see subsection on $Co(NH_3)_3$] is charged with an excess of dry $Ni(SCN)_2$. Then a solution of KNH_2 in liquid NH_3 is added. A flocculent red precipitate forms; this is washed with liquid NH_3 until peptization just starts. The product is transferred to an auxiliary apparatus (as in the procedure on p. 1527) and dried in high vacuum at 40°C.

Used for the preparation of Ni_3N_2.

PROPERTIES:

Red powder. Reacts mildly with H_2O to form $Ni(OH)_2$ and NH_3. Decomposes when heated in vacuum to 120°C.

REFERENCE:

G. S. Bohart. J. Phys. Chem. 19, 537 (1915).

Trinickel Dinitride

$$Ni_3N_2$$

$$\underset{272.3}{3\,Ni(NH_2)_2} = \underset{204.1}{Ni_3N_2} + \underset{88.8\,l.}{4\,NH_3}$$

Nickel (II) amide (see preceding preparation) is heated in vacuum at 120°C; NH_3 is slowly evolved and Ni_3N_2 is formed. Some N_2 is also produced in a side reaction.

Alternate method: A mixture of 10 parts of NiO and 7.4 parts of completely anhydrous $Ni(CN)_2$ is fused in an electric arc surrounded by pure N_2 [A. C. Vournasos. Comptes Rendus Hebd. Séances Acad. Sci. 163, 889 (1919)].

DropBooks

PROPERTIES:

Black powder. Reacts very slowly with water. Decomposes to Ni and N_2 above 120°C. Alkalies liberate NH_3.

REFERENCE:

G. S. Bohart. J. Phys. Chem. 19, 537 (1915).

Trinickel Nitride

$$Ni_3N$$

$$\underset{176.1}{3\,Ni} + \underset{22.4\,l.}{NH_3} = \underset{190.1}{Ni_3N} + \underset{33.6\,l.}{1\tfrac{1}{2}\,H_2}$$

An alumina boat is charged with 20 mg. of nickel obtained from $Ni(CO)_4$. The boat is heated for three hours at 445°C in a reaction tube through which flows a stream of NH_3 (22 cm./sec.). The preparation is cooled in the NH_3 stream, ground carefully in an agate mortar, and allowed to react with NH_3 once more under the same conditions.

The test for N in the product may be made by the micro-Kjeldahl method.

PROPERTIES:

Black-gray powder. d_4^{25} 7.66. Unaffected by moisture and O_2. Dissolved slowly by dil. mineral acids in the cold, rapidly by conc. HCl and conc. HNO_3. Dissolved rapidly by all hot acids. Not attacked by aqueous NaOH. Crystal structure: hexagonal close packing of Ni atoms, oriented incorporation of N.

REFERENCE:

R. Juza and W. Sachse. Z. anorg. allg. Chem. 251, 201 (1943).

Nickel Carbide

Ni_3C

$$\underset{176.1}{3\,Ni} + \underset{44.8\,l.}{2\,CO} = \underset{188.1}{Ni_3C} + \underset{22.3\,l.}{CO_2}$$

Pure NiO is reduced with pure H_2 at 275–285°C until constant weight. The fine Ni powder is heated at once with pure CO (completely free of O_2) for 260 hours at 270°C. The Ni_3C thus produced is pyrophoric. This may be remedied by heating for a long time in O_2-free nitrogen at 250°C and cooling in the N_2 stream.

Test for bound C: Heating with pure H_2 at 250–270°C evolves C as CH_4.

PROPERTIES:

Gray-black powder. d_4^{18} 7.97. Heat of formation: —9.2 kcal. per mole. Decomposed at room temperature by conc. and dil. HCl; precipitation of C does not occur (see Fe_3C). Soluble in dil. HNO_3; dil. H_2SO_4 causes separation of C. Stable at temperatures up to 380–400°C. Crystal structure: hexagonal close packing of Ni atoms.

REFERENCE:

H. A. Bahr and Th. Bahr. Ber. dtsch. chem. Ges. 61, 2177 (1928).

Nickel (II) Carbonate

$NiCO_3 \cdot 6\,H_2O$

Prepared by electrolysis of CO_2-saturated H_2O with nickel electrodes.

An electrolysis cell (20 × 15 × 20 cm.) is covered with a wooden lid from which three pieces of nickel sheet electrodes (20 × 12.7 × 0.05 cm.) are suspended. Two of the electrodes are placed at the sides of the vessel and are interconnected; the third is in the center and serves as the anode. The cell is filled with conductivity water to 2.5 cm. below the top, pure CO_2 is bubbled through, and the current is turned on and controlled at 2–2.2 amp. The cell is cooled externally with running water. The $NiCO_3 \cdot 6H_2O$ drops to the bottom. It is filtered off and dried at 100°C. The yield is about 30 g./day.

PROPERTIES:

Formula weight 226.82. Pale-green rhombohedra or monoclinic prisms. Readily soluble in acids. The product prepared in the above manner is free of alkali, but contains some black hydroxide.

REFERENCE:

E. C. C. Baly and N. R. Hood. Proc. Roy. Soc. London 122, 313 (1929).

$NiCO_3$

DropBooks

Anhydrous $NiCO_3$ exists in two forms, one green (I) and one yellow (II).

GREEN FORM (I):

A solution of 0.12 moles of $NiCl_2$ in 100 ml. of water is acidified with HCl and charged into an autoclave. At 250°C and a CO_2 pressure of 1700 p.s.i., a solution of 0.18 moles of $NaHCO_3$ in 100 ml. of water is added dropwise. Green, crystalline $NiCO_3$ precipitates. Yield: 25–30%.

YELLOW FORM (II):

The yellow $NiCO_3$ forms under the same conditions as the green, but at a temperature of 180°C and from very conc. solutions (0.22 moles of $NiCl_2$ in 25 ml. of water and 0.38 moles of $NaHCO_3$ in 100 ml. of water). The yield is poor. At lower temperatures only colloidal products are obtained; at temperatures between 180° and 250°C a mixture of I and II is produced.

PROPERTIES:

The green form consists of microscopically small, transparent, doubly refracting green rhombohedra; it is not attacked by warm

oxalic acids or by boiling water. The habit and physical and chemical properties of II are the same as those of I. On heating to approximately 400°C, both carbonates decompose to CO_2 and green NiO. Both crystallize as rhombohedra.

REFERENCE:

R. de St. Léon Langlés. Ann. Chimie 7, 568 (1953).

Nickel (II) Thiocyanate

$Ni(SCN)_2$

Prepared by dissolving $Ni(OH)_2$ in a dilute HNCS solution and evaporating the resulting solution of $Ni(SCN)_2$.

A dilute HNCS solution is saturated with $Ni(OH)_2$ or nickel carbonate and the deep-green solution is evaporated at about 15°C. Large green crystals of $Ni(SCN)_2 \cdot 4H_2O$ are deposited. Above 15°C and on drying of $Ni(SCN)_2 \cdot 4\ H_2O$, a yellow powder of $Ni(SCN)_2 \cdot 0.5\ H_2O$ is obtained. It can be rendered anhydrous by heating to 150°C.

PROPERTIES:

Formula weight 174.88. Dark chocolate-colored powder. On addition of water, becomes first yellow and then dissolves with a green color.

REFERENCES:

A. Rosenheim and R. Cohn. Z. anorg. Chem. 27, 280 (1901); Ber. dtsch. chem. Ges. 33, 1111 (1901); A. de Sweemer. Natuurwetensch. Tijdschr. 14, 231 (1932).

Di-μ-sulfido-tetrakis(dithiobenzoato)dinickel (IV)

$(C_6H_5 \cdot CSS)_2NiS_2Ni(SSC \cdot C_6H_5)_2$

This nickel (IV) complex compound is obtained by oxidation of the corresponding nickel (II) complex compound with O_2.

An alcoholic solution of 1 mmole (0.13 g.) of $NiCl_2$ is treated with an alcoholic solution of 12 mmoles (0.15 g.) of monothiobenzoic acid and 6 mmoles (0.24 g.) of NaOH. The clear yellow-brown solution (in which the Ni is present as $[Ni(SCOC_6H_5)_4]^{2-}$) is refluxed at 50°C, and at the same time a gentle stream of O_2 is introduced. The oxidation is shown by a change in color, first to red and then to violet. The reaction is complete in about four

hours. The dark-violet compound is filtered off, washed with alcohol and water, and recrystallized from benzene.

PROPERTIES:

Formula weight 794.55. Tuft-shaped aggregates of dark-violet crystals. May be recrystallized from benzene, alcohol, ether and CS_2. Very stable to acids and bases; decomposed only by oxidizing acids.

REFERENCE:

W. Hieber and R. Brück. Z. anorg. allg. Chem. 269, 26 (1952).

Potassium Tetracyanonickelate (II)

$$K_2[Ni(CN)_4] \cdot H_2O$$

$$\underset{(6\,H_2O)}{NiSO_4} + 2\,KCN = Ni(CN)_2 + K_2SO_4$$

$$\underset{262.9}{} \quad \underset{130.2}{} \quad \underset{110.7}{} \quad \underset{174.3}{}$$

$$Ni(CN)_2 + 2\,KCN + H_2O = K_2[Ni(CN)_4] \cdot H_2O$$

$$\underset{110.7}{} \quad \underset{130.2}{} \quad \underset{18.0}{} \quad \underset{259.0}{}$$

DropBooks

A solution of 60 g. of $NiSO_4 \cdot 6\,H_2O$ in 200 ml. of water is prepared, and a solution of 29.7 g. of KCN in 70 ml. of water is added slowly, with constant stirring. The gray-green precipitate of $Ni(CN)_2$ is washed until free of sulfate and then filtered off.

The solid $Ni(CN)_2$ is placed in a solution of 29.2 g. of KCN in about 30 ml. of water. The solution, which is now red, is heated on a hot plate until small crystals appear. These are redissolved and the solution is allowed to cool. The compound precipitates as beautiful crystals. The yield is 57.4 g. (97%).

SYNONYM:

Potassium nickel (II) cyanide hydrate.

PROPERTIES:

Orange-red crystals. The water of hydration is completely removed by heating to 100°C. Very soluble, even in cold water; decomposed to $Ni(CN)_2$ by mineral acids. Forms black precipitates of higher nickel hydroxides on addition of hypobromites.

REFERENCE:

W. C. Fernelius and J. J. Burbage in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 227.

SECTION 29

The Platinum Metals

H. L. GRUBE

Pure Platinum

Pt

Platinum obtained from Russian or Colombian platinum ores or by industrial recovery processes contains the other platinum metals as impurities, as well as gold, iron and copper.

The following methods are recommended for its purification: the lead fusion process, based on the analytical procedures of Saint-Claire-Deville and Stas, and the caustic soda precipitation of Schneider [1] and Seubert [2], in which all the platinum metals except Pt pass into their lower oxidation states, which are not precipitated by NH_4Cl. There is also the Finkener process, based on recrystallization of Na_2PtCl_6 from dilute soda solutions; this has been described by Mylius and Förster [3]. However, this method leads to poor yields because of the low solubility of Na_2PtCl_6. A process by Reerink [4] makes use of platinum's ability to form a volatile carbonyl chloride with Cl_2 and CO.

The hypochlorite method developed by Mylius and Mazzucchelli [5] for the preparative purification of the platinum metals can be recommended as a laboratory procedure. Platinum (in the form of small foil clippings or sponge) is dissolved in the purest aqua regia available (glass or porcelain vessels); the solution is withdrawn (or decanted) and carefully evaporated in a porcelain dish over a small flame; the concentrate is dissolved in hydrochloric acid and hot H_2O. The chloride solution is diluted with a large amount of water, heated to about 80°C, and made slightly alkaline with soda. Any IrO_2 present is precipitated with Cl_2, bubbled through for a short time. The initially colloidal iridium-containing precipitate coagulates after a short time to a black flocculent deposit which settles rapidly in the yellowish-red solution. Addition of a few milliliters of alcohol produces a marked increase in the speed of separation. The more carefully the solution is neutralized (without, however, going below a pH of 7), the more complete is the separation of the unwanted oxide.

The other platinum metals, gold and the heavy base metals may be precipitated as the oxides by addition of hypochlorite. This reaction can therefore be used for the removal of all metallic impurities. The only oxide soluble in an excess of hypochlorite is the black RuO_2 (it is thereby converted to the volatile RuO_4).

The filtered platinum solution is heated in a beaker or porcelain vessel and treated with NH_4Cl. The $(NH_4)_2PtCl_6$ deposit is then filtered off and extracted by boiling with distilled water to dissolve any small quantities of $(NH_4)_2PdCl_6$ still remaining.

The very pure platinum obtained after ignition is free of all the other platinum metals, gold and the heavy base metals. If the Pt still contains a few tenths or hundredths of a percent of Ir, the purification process can be repeated.

REFERENCES:

1. W. von Schneider. Liebigs Ann. 5, 271 (1997).
2. K. Seubert. Ibid. 207, 8 (1881).
3. F. Mylius and F. Förster. Ber. dtsch. chem. Ges. 25, 665 (1892).
4. E. H. Reerink. Z. anorg. allg. Chem. 173, 45 (1928).
5. F. Mylius and A. Mazzucchelli. Ibid. 89, 1 (1914).

DropBooks

Reclaimed Platinum

In order to reclaim platinum residues from the laboratory (e.g., platinum absorbed on filter papers, scraps, filter ash, etc.), these are well ignited and then sieved through a fine screen, separating the residues into "fine" and "coarse" fractions.

The coarse fraction remaining on the screen contains the metallic residues, such as small pieces of wire, small clippings and pieces of foil. It is advisable to pass a magnet through this material to locate and remove any iron present in the form of nails, wire, etc. In some cases, it may be advisable to extract the iron from this fraction by boiling with dilute hydrochloric acid. Copper or brass residues are extracted by boiling with dilute nitric acid. The coarse material is then dissolved in aqua regia and processed to recover the Pt and its associated metals. In order to expel the nitric oxides present, the aqua regia solution is evaporated to a sirupy thickness, taken up with water and some dil. hydrochloric acid, and treated with NH_4Cl to precipitate the $(NH_4)_2PtCl_6$. The Pt still remaining in the mother liquor is precipitated with pure Zn.

The iron in the fine fraction is first extracted by boiling with dilute hydrochloric acid; after ignition, the residue is dissolved by heating in aqua regia. This solution is evaporated to a sirupy

thickness and taken up with H_2O and HCl; the Pt is precipitated as $(NH_4)_2PtCl_6$.

If aged solutions or more or less reduced salts and preparations are to be processed, Berthold's work-up method is recommended. Often dirt appears in the residue on long standing, and sometimes the Pt salts are partially reduced by alcohol on long storage. In either case the liquid is first filtered, the residue is treated with aqua regia to dissolve any platinum it may contain, and the resulting solution is filtered.

The last filtrate is not combined with the first one, but is evaporated to drive off the aqua regia. The residue is extracted with hot water and this solution added to the main (that is, the first) filtrate.

When the solution to be worked up originates from an analytical laboratory, the main impurities are likely to be salts of K, Na, Mg and NH_4. Alcohol and ether may also be present. In this case, the liquid is treated with some conc. HCl and pure Zn. If K_2PtCl_6 precipitates, it must be reduced by heating to convert it into soluble material. Any alcohol or ether present must first be driven off.

After the reduction, which is clearly indicated by the decoloration of the liquid, the supernatant is decanted; the residue is thoroughly extracted by boiling with conc. HCl and washed by decantation with hot distilled water until the wash water no longer contains any chloride.

Double salts containing a platinum and an alkali metal ion (and especially the ammonium ion) are best treated by careful calcination in a Pt crucible under a layer of NH_4Cl, extraction with boiling water acidified with some hydrochloric acid, and reignition.

For reclaiming procedure for Pt from electrolytic Pt baths, see p. 1567.

REFERENCE:

A. Berthold. Z. angew. Chem. 14, 621 (1901).

Platinum Sponge

Platinum sponge is best produced by prolonged ignition of $(NH_4)_2PtCl_6$ in a Pt dish or bowl (dull red heat, about 600°C). The ignited sponge should be boiled with dilute hydrochloric acid, and then with distilled H_2O. Finally it is gently heated again in a Pt dish.

Platinum Black

Of the various methods of preparation given in the literature, that described by Gutbier and Maisch seems to be the best. A 5%

solution of H_2PtCl_6 is heated, neutralized with Na_2CO_3, and poured into a boiling solution of sodium formate. The black residue which precipitates immediately is washed by decantation with hot H_2O. It is then filtered off with suction and freed from residual water by pressing between filter papers; it is further dried over P_2O_5 or conc. H_2SO_4.

PROPERTIES:

Black powder, very active toward H_2, with a maximum absorptive capacity for H_2 at 0°C.

REFERENCE:

A. Gutbier and O. Maisch. Ber. dtsch. chem. Ges. 52, 1370 (1919).

Platinized Asbestos

Asbestos is saturated with an alcoholic solution of $H_2PtCl_6 \cdot 6\ H_2O$ (technical "platinum chloride"), thereby producing a material with a definite platinum concentration. In view of the cost of the solution, the calculated quantity of H_2PtCl_6 must be absorbed quantitatively by the asbestos; it is therefore essential to establish accurately (by preliminary experiments) the absorbance of the asbestos to be used. The H_2PtCl_6-saturated asbestos is kneaded as uniformly as possible and the mass is ignited while being agitated with a Pt spatula or rod. This method is particularly suitable for producing asbestos with low Pt contents (0.1–1% Pt). Its advantage lies in that the product contains no foreign salts which could obstruct the pores of the asbestos fibers and adversely affect its catalytic activity.

To prepare platinized asbestos with high platinum contents (5–10%), the mass is saturated with a H_2PtCl_6 solution which does not contain alcohol. The procedure is the same as described above. The mass is made slightly alkaline by treating it with dil. sodium hydroxide, and the chloride is then reduced to fine, particulate Pt with sodium formate. The reduction is best carried out in a muffle furnace at about 300–400°C. Finally the asbestos is freed of alkali salts by thorough washing with cold water and is dried in a muffle furance. At this point the asbestos should be light gray.

Erdmann gives another method. Asbestos saturated with conc. H_2PtCl_6 is placed in a conc. solution of NH_4Cl. The asbestos, which is thus permeated with $(NH_4)_2PtCl_6$, is placed on a glass funnel to allow the excess solution to drain, and is then slowly heated to incandescence. This produces an asbestos with a high concentration of platinum sponge; however, the uniformity of the product leaves much to be desired.

For analytical purposes the platinized asbestos fibers should be as short as possible (almost powdery). For large-scale catalytic processes, the fibers should, on the other hand, be as long as possible.

REFERENCE:

O. Erdmann. Lehrb. d. anorg. Chem. [Inorganic Chemistry Text], 5th ed., p. 175 (1910).

Handling of Platinum Equipment

Because the various chemicals used in ignition and melting processes may be corrosive, certain precautions must be observed in using platinum apparatus. Unfortunately, the use of platinum as vessel material is not a panacea for all the corrosion problems that plague the chemist.

Materials which readily form alloys with Pt (nonmetals P, As, Te, Si, B and C) or metals which melt at low temperatures (Pb or Sn) or substances which liberate these materials during ignition or melting processes can not only damage but even destroy platinum apparatus. This also holds for all melts containing potassium hydroxide, sodium nitrate, or mixtures of the alkali hydroxides or alkali carbonates with sodium nitrate; melts containing peroxides, cyanides or sulfides are particularly injurious to crucibles.

In general, ignitions should not be carried out at unnecessarily high temperatures or with reducing flames; reduction with an acetylene flame is forbidden.

Reducing conditions involving burner or flue gases, activated charcoal and the like are particularly deleterious when free silicic acid is also present. In this case, platinum-silicon alloys are formed, leading to the characteristic silicon fracture.

The critical corrosion temperature, i.e., the temperature above which serious corrosion occurs, generally lies around 700°C. However, this temperature is about 500-600°C for melts consisting mainly of KOH, $Ba(OH)_2$, peroxides or cyanides; for melts composed mainly of carbonates or neutral salts, it is 800°C or somewhat higher. Further details are given in the Mitteilungen aus dem Chem. Laboratorium, W. C. Heraeus Co., Hanau; publications of the Engelhardt Industries, Newark, N. J.; G. Bauer, Chemiker-Ztg. 62, 257 (1938).

CLEANING

Careful treatment of Pt vessels after use is essential. Usually the crucible contents can be easily removed by mechanical means.

In some cases, the contents can be dissolved with warm hydrochloric acid or chlorine-free nitric acid. If this does not suffice, sodium pyrosulfate is heated in the Pt crucible until liberation of SO_3, the molten liquid is poured out, and the material still adhering to the walls is dissolved with hot water (O. Brunck). The crucible is not damaged at all by this treatment. If the edges of the crucible lid become bent out of shape, they can be smoothed out against a glass plate with a spatula made of horn or plastic. A very badly dented crucible should best be repaired by a goldsmith or other expert.

A Pt crucible that develops a small tear due to careless handling can readily be repaired in the laboratory. A small piece of thin gold foil of suitable size and shape is placed over the tear, and the spot is heated with an oxyhydrogen torch until the gold melts, after which the patch is smoothed with a burnisher. Such a crucible can still be used for most purposes. Very small tears can be healed with an oxyhydrogen torch; there is no need for a patch material in this case. Platinum wires, e.g., the leads to thermocouples or electrodes, can also be welded together quite simply with an oxyhydrogen torch: the two wires to be joined are laid close together and fused, or are welded together at a slightly lower temperature by a light tap with a hammer.

In case of serious damage, however, it is advisable to have the vessel repaired by a specialist.

DropBooks

Platinum Electroplating

Thin layers of platinum can easily be deposited from electrolytic baths; however, the deposition must be repeated several times to produce thicker deposits.

Böttger gives a very good bath formula: it consists of a solution of $(NH_4)_2PtCl_6$ in sodium citrate. Langbein gives the following instructions for preparing this bath: 500 g. of citric acid is dissolved in two liters of H_2O and neutralized with sodium hydroxide. This solution is heated to boiling and the $(NH_4)_2PtCl_6$, freshly precipitated from a solution of 75 g. of dry H_2PtCl_6, is added with stirring; the mixture is heated until the $(NH_4)_2PtCl_6$ is completely dissolved; the solution is then cooled and diluted with H_2O to five liters. To reduce the electrical resistance of the bath, 4–5 g. of NH_4Cl is added per liter.

The electrolysis proceeds at 3–4 volts, a current density of 0.065 amp./in.^{2} and a temperature of 70–90°C. Thin Pt sheet is always used as the anode in platinum plating baths; it is scarcely attacked at all. The bath must always be kept slightly alkaline; if this is no longer the case after prolonged passage of current, dilute aqueous ammonia is added until an odor of ammonia is

noticeable. If the bath is acid, Pt sponge will rapidly precipitate.

C. W. Keitel et al. give another bath formula: cis-dinitrodiammineplatinum is dissolved in ammonia, and ammonium nitrate and sodium nitrite are added to improve the conductivity of the bath.

Objects to be plated with platinum (cathodes) are prepared in exactly the same way as in any other method of electroplating. Given the cost of platinum, these objects are usually small; platinum electrolysis vessels therefore need to hold only a few liters of the solution; the vessel will thus usually be a glass or porcelain beaker or a small iron trough coated on the inside with a special alkali- and acid-resistant enamel. If the platinum deposit is too dull, it can be rubbed and scoured in the same way as gilt-ware, and then replaced in the platinum bath to deposit a further platinum layer; this treatment may be repeated until the required deposit thickness is reached.

The current efficiency in platinum coating is very small (only 30-40% of the theoretical) since large quantities of energy are consumed in liberating the great amount of H_2 that evolves. This H_2 also hardens the platinum deposits.

REFERENCE:

Pfanhauser et al. Galvanotechnik [Applied Electrochemistry], Leipzig, 1949, pp. 939-942; gives further details on bath compositions and on other recently developed plating baths.

According to Lummer and Kurlbaum, the liquid most suitable for the platinization of electrodes for potential measurements consists of 3 g. of $H_2PtCl_6 \cdot 6\ H_2O$ plus 0.10 g. of lead acetate in 97 ml. of H_2O; the bath temperature is 20-30°C, the potential about 4 volts. Two series-connected storage batteries are used as a power source and the current is regulated to produce a moderate gas evolution. The current is reversed, so that each electrode serves alternately as the anode and cathode. The total time for initial platinization is 10-15 minutes; usually only 1-2 minutes is sufficient for replating electrodes already covered with platinum black (before platinum plating these electrodes must be carefully cleaned; it is best to do this with chromosulfuric acid).

A thin coat of platinum (burnished platinum) can be produced on glass and porcelain by baking on either of the following special solutions:

I. A solution of 1 g. of platinic chloride ($H_2PtCl_6 \cdot 6\ H_2O$) in 3.5 ml. of absolute alcohol is mixed with 10 ml. of a concentrated alcoholic solution of boric acid and 25 ml. of a solution of Venetian turpentine in lavender oil.

II. A solution of 1 g. of platinic chloride ($H_2PtCl_6 \cdot 6\ H_2O$) in the minimum amount of absolute alcohol is added slowly (stirring) to

6 ml. of ice-cold lavender oil. After warming, Burgundy pitch is added to the mixture to give the required consistency.

In either case, the platinum-containing mass is spread uniformly on the glass (or porcelain) and carefully heat-dried so that no bubbles develop. The coated surface is then heated to a dull red heat in a muffle furnace or in a sulfur-free blowtorch flame.

The ingredients of these solutions are not usually available in the laboratory. However, ready-for-use solutions for producing burnished platinum (with instructions) are provided by companies handling noble metals (e.g., W. C. Heraeus of Hanau or Degussa of Frankfurt or Engelhardt Industries of Newark, N. J.).

REFERENCE:

Ostwald-Luther. Physiko-Chemische Messungen [Physicochemical Measurements], 4th ed., Leipzig, 1925, pp. 156-159.

RECLAIMING PLATINUM FROM USED BATHS

If the liquid quantity is not too large, then the best method is to precipitate the platinum with H_2S (this is preferred over the procedure involving concentration of the solution and reduction of the residue to the metal). The platinum can be precipitated from larger liquid quantities with pure Zn (following acidification of the bath liquid).

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Platinum Chlorides

Streicher and Krustinsons gives the following facts about the stability of chlorides of platinum as a function of temperature at 1 atm. of Cl_2 pressure:

$PtCl_4$ (russet) stable up to 382°C,

$PtCl_3$ (dark green) stable between 382 and 435°C,

$PtCl_2$ (greenish brown) stable between 435 and 515°C.

The existence of PtCl (pale yellow-green), 581-583°C, is not altogether certain.

REFERENCES:

S. Streicher. Thesis, Univ. of Darmstadt, 1913; J. Krustinsons, Z. Elektrochem. 44, 537 (1938).

$PtCl_4$

Prepared by decomposition of $H_2PtCl_6 \cdot 6\ H_2O$ in a stream of chloride. The starting material is placed in a boat set in a

combustion tube made of high-melting glass. The temperature is increased slowly from 60 to 150°C, which drives off water. When the material is completely dry, the temperature is raised to 275-300° over a period of two hours, and held at this level for 0.5 hour. The temperature must not be allowed to rise above 360°C. After cooling to about 150°C, the product is removed, quickly ground, replaced in the combustion boat, and reheated for 0.5 hour at 275°C while a stream of Cl_2 is passed over it. The resultant chloride is placed, while still hot, in a hermetically closable storage bottle. The yield from 6 g of $H_2PtCl_6 \cdot 6\ H_2O$ is 3.7 g. of $PtCl_4$.

PROPERTIES:

Red-brown, very hygroscopic crystals. Very soluble in water, sparingly soluble in alcohol. Absorbs moisture on standing in air, yielding $PtCl_4 \cdot 5\ H_2O$.

REFERENCES:

A. Gutbier. Z. anorg. Chem. 81, 381 (1913); M. S. Kharasch and T. A. Ashford. J. Amer. Chem. Soc. 58, 1736 (1936); R. N. Keller in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 247.

$PtCl_2$

I. Prepared by heating platinum sponge to about 500°C in a stream of Cl_2 or, better, by thermal decomposition of $PtCl_4$ or $H_2PtCl_6 \cdot 6\ H_2O$.

The $H_2PtCl_6 \cdot 6\ H_2O$ (or the commerical product containing 40% Pt) is subjected to a preliminary decomposition over a free flame at 150°C. The resulting residue is ground and decomposed in a slow air stream at 360°C. Depending on the quantities involved, the operation may require several hours. At the end the undecomposed H_2PtCl_6 should be removed by extracting and washing with H_2O, after which the product is redried at 360°C.

PROPERTIES:

Formula weight 266.0. Greenish-brown powder. Insoluble in water. At 250°C, dry $PtCl_2$ forms a very volatile carbonyl chloride with CO. Thus gases containing CO should not be used in reductive ignition of platinum chloride (the same holds for the chlorides of the other platinum metals). Very sparingly soluble in dil. hydrochloric acid, yielding H_2PtCl_4.

REFERENCE:

M. S. Kharasch and T. A. Ashford. J. Amer. Chem. Soc. 58, 1776 (1936).

II. A chocolate-brown form of platinum (II) chloride can be prepared by careful concentration of a solution of tetrachloroplatinic (II) acid (see p. 1570) in hydrochloric acid; this material is more soluble in hydrochloric acid and aqueous ammonia than the product obtained by method I.

REFERENCE:

W. E. Cooley and D. H. Busch in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 208.

Hexachloroplatinic (IV) Acid

$H_2PtCl_6 \cdot 6\,H_2O$

Obtained by dissolving platinum in aqua regia. To prepare large quantities, the platinum, in the form of thin shavings of foil, is dissolved in a porcelain or glass vessel and the solution poured into a porcelain dish. Hydrochloric acid is added and the solution evaporated to sirupy consistency in order to drive off the nitric acid and any $PtCl_4 \cdot 2\,NOCl$ which may form. The thick solution is taken up with HCl and the resulting solution reevaporated to a sirup. This is repeated several times. Since the last traces of nitric oxide are very difficult to remove, finely divided Pt may also be dissolved in hydrochloric acid through which Cl_2 is bubbled (or nascent Cl_2 may be generated in the solution itself by carefully adding $HClO_3$ or H_2O_2 to it).

The concentrated solution is placed in a large tared dish and the percentage of platinum in the chloride is adjusted (usually to 39.5 or 40%) by controlled evaporation of the acid on a burner (check on the decrease in weight).

When the required percentage of platinum is reached, the dish is removed from the burner and allowed to stand until the chloride solution becomes a definite slurry. The solution is then stirred with a thick glass rod until it is completely cool.

SYNONYMS:

Chloroplatinic acid, platinum chloride, platinic chloride.

PROPERTIES:

Formula weight ($H_2PtCl_6 \cdot 6\,H_2O$) 518.0. Commercial "platinum chloride" containing 39.5–40% Pt is not a definite hydrate, but has the composition of $H_2PtCl_6 \cdot 4.5\,H_2O$ and is deep orange. Starting material for the preparation of most platinum compounds.

Tetrachloroplatinic (II) Acid

H_2PtCl_4

Stable only in solution; prepared by reduction of H_2PtCl_6 with a stoichiometric quantity of $N_2H_4 \cdot 2\,HCl$:

$$2\,H_2PtCl_4 \cdot 6\,H_2O + N_2H_4 \cdot 2\,HCl \rightarrow 2\,H_2PtCl_4 + N_2 + 6\,HCl + 12\,H_2O$$

Commercial platinum chloride (10 g., 40% Pt) is dissolved in 50 ml. of water in a 150-ml. beaker. Then 1.07 g. of solid $N_2H_4 \cdot 2\,HCl$ is added in small portions, so that the solution effervesces each time due to evolution of N_2. Within five minutes of adding the last of the hydrazine salt, the deep red solution is heated on a steam bath until no further gas evolves; it is then filtered to remove the small quantity of platinum black which may deposit out.

PROPERTIES:

Red solution; leaves a brown deposit of $PtCl_2$ on careful evaporation. Very stable in hydrochloric acid solution. With an excess of ammonia it forms $[Pt(NH_3)_4]\,[PtCl_4]$ or $[Pt(NH_3)_4]Cl_2$.

REFERENCE:

W. E. Cooley and D. H. Busch in: T. Moeller, Inorg. Syntheses, Vol. V, New York-Toronto-London, 1957, p. 208.

Ammonium Hexachloroplatinate (IV)

$(NH_4)_2PtCl_6$

A dilute, weakly acidic (HCl) solution of H_2PtCl_6 is prepared and, if that is needed, oxidized with H_2O_2. It is then reacted with an excess of NH_4Cl (at least three parts by weight of NH_4Cl to one of Pt) and slowly evaporated to dryness on a steam bath. The salt crust mixed with the resulting residue is broken up with a glass rod and the solids heated on a steam bath with continuous stirring until the powdery mass no longer gives off the odor of HCl. The dry residue is then carefully moistened with some distilled water, taken up in cold saturated NH_4Cl solution and filtered. It is washed first with NH_4Cl solution, then with alcohol. The mother liquor should be completely colorless and show only traces of Pt on reaction with H_2S and $SnCl_2$.

SYNONYMS:

Platinic salammoniac, ammonium platinichloride, ammonium chloroplatinate.

PROPERTIES:

Formula weight 443.9. Lemon-yellow octahedra. A color of yellow ochre to brick red instead of lemon yellow indicates the presence of other platinum metals, particularly Pd, Ir and Ru. Greenish-yellow to green indicates that Rh is present. Completely decomposed on ignition in a platinum dish, leaving fine particles of platinum sponge. Very sparingly soluble in H_2O, less soluble in NH_4Cl solutions. Solubility (15.5 °C) 0.67 g., (100 °C) 1.25 g./100 ml. H_2O. Colorless solution in conc. ammonia. Like K_2PtCl_6, insoluble in alcohol.

Potassium Hexachloroplatinate (IV)

K_2PtCl_6

Prepared by adding a solution of KCl to H_2PtCl_6 (the ratio of solid components is 3 : 1). For complete precipitation of the Pt with KCl or NH_4Cl, the Pt must be completely oxidized to the +4 state and the solution must be as concentrated as possible; however, the solution should not be so concentrated that it becomes viscous while the product is being formed.

SYNONYM:

Potassium platinichloride.

PROPERTIES:

Formula weight 486.0. Pure yellow crystals; dissolve with difficulty in water; insoluble in alcohol. The color changes in the presence of the other platinum metals in the same way as does that of $(NH_4)_2PtCl_6$. Solubility in water:

°C	g. K_2PtCl_6/100 g. H_2O
0	0.74
10	0.90
20	1.12
50	2.16
80	3.79
100	5.13

Sodium Hexachloroplatinate (IV)

Na_2PtCl_6, $Na_2PtCl_6 \cdot 6\,H_2O$

Prepared by passing Cl_2 over a mixture of platinum sponge with twice its weight of NaCl. The reaction temperature should be higher

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than 500°C, but should not under any circumstances exceed 660°C. Purification is effected by solution of the product in alcohol, filtration to remove NaCl and platinum metals, and concentration of the solution, after which the salt is dried in a drying oven.

If the reaction mixture is dissolved in water (instead of alcohol) and the solution concentrated, $Na_2PtCl_6 \cdot 6\,H_2O$ is produced as triclinic, orange-colored crystals. A very pure salt is obtained by recrystallization from 1% soda solution; it loses its water of crystallization below 100°C.

SYNONYM:

Sodium platinichloride.

PROPERTIES:

Formula weight (anhydrous) 453.8. Orange crystals. Soluble in water and alcohol.

REFERENCE:

L. Wöhler and P. Balz. Z. anorg. allg. Chem. 149, 356 (1925).

Potassium Tetrachloroplatinate (II)

K_2PtCl_4

Prepared by reduction of K_2PtCl_6 with SO_2 or $N_2H_4 \cdot 2\,HCl$.

I. A suspension of 4.7 g. of K_2PtCl_6 in 35 ml. of H_2O is prepared in a 50-ml. beaker; small portions of freshly prepared SO_2 solution are added while stirring the suspension mechanically and heating it to 85–90°C on a water bath. About 15 additions of 0.6 ml. should be made first, followed by 10–15 additions of 0.4 ml. After each addition, 2–3 minutes (later 3–4 minutes) should be allowed until the SO_2 is consumed and its odor disappears. Toward the end of the reduction, when the suspended particles are gradually disappearing, it is necessary to proceed even more slowly. The solution remaining on complete reduction is concentrated on a water bath until crystallization begins. After cooling, it is suction-filtered, and the red K_2PtCl_4 is dissolved in 40 ml. of cold water, filtered to remove any small residue of K_2PtCl_6, and the residue rinsed with 5 ml. of water. The solution is carefully transferred (rinsing with 10 ml. of water) into an 800-ml. beaker; its total volume at this point is 55–60 ml. Then 660 ml. of a 1:1 mixture of acetone and ether is added with stirring. This precipitates the solid chloroplatinate,

which is allowed to settle. The bright yellow liquid is decanted, and the salt is washed three times with 120 ml. of acetone–ether mixture (decantation) and then three times with 80 ml. of ether. After filtering and drying the product in air, the salt is recrystallized from hot, slightly acidified water.

II. The K_2PtCl_6 can be reduced with $N_2H_4 \cdot 2\,HCl$ in the same way as H_2PtCl_6.

$$\underset{972.1}{2\,K_2PtCl_6} + \underset{105.0}{N_2H_4 \cdot 2\,HCl} = \underset{830.2}{2\,K_2PtCl_4} + 6\,HCl + N_2$$

The K_2PtCl_6 is suspended (brisk stirring) in 10–12 times its weight of water. With continuous stirring, the stoichiometric quantity of solid $N_2H_4 \cdot 2\,HCl$ is added in small portions, the temperature being raised to 50°C within 10 minutes. The K_2PtCl_6 dissolves with evolution of N_2. The solution is brought to the boiling point, filtered and concentrated, first over an open flame and then on a water bath, until crystallization begins. Since no foreign ions are introduced in this preparative method, recrystallization can be omitted, provided the starting materials used are pure.

An excess of $N_2H_4 \cdot 2\,HCl$ leads to the formation of platinum black, while a deficiency leaves undissolved K_2PtCl_6.

The compounds $(NH_4)_2PtCl_4$ and Na_2PtCl_6 can also be prepared in this way.

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PROPERTIES:

Formula weight 415.1. Red crystals or bright red powder. Solubility in water (16°) 0.93 g., (100°C) 5.3 g./100 ml. Insoluble in alcohol; reduced in alcohol.

REFERENCES:

I. Magnus, Pogg. Ann. 14, 241 (1828).
II. R. N. Keller in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York–London, 1946, p. 247; N. G. Klyuchnikov and R. N. Savel'eva, abstract in Chem. Abs. 51, 10288 (1957).

Platinum (II) Oxide

PtO

Wöhler's method is recommended in preference to others. Oxygen is passed at 150°C over platinum sponge that is as finely divided as possible; the temperature must not exceed 560°C.

PROPERTIES:

Completely anhydrous black powder. Readily soluble in aqua regia. Instantly reduced by H_2 at ordinary temperatures, liberating heat and forming gray platinum sponge. Decomposes at atmospheric pressure (560°C): $2\ PtO = 2\ Pt + O_2$.

REFERENCE:

L. Wöhler, Z. Elektrochem. 15, 136 (1909).

Platinum (IV) Oxide

$PtO_2 \cdot xH_2O$

I. It is impossible to prepare completely anhydrous PtO_2 without decomposing it. In addition, even the hydrated material (which contains variable quantities of water) is not easy to obtain in pure form. The procedure of Wöhler and Frey appears to be the most suitable. Red-brown hydrated platinum dioxide is precipitated by boiling a pure, concentrated solution of H_2PtCl_6 with concentrated Na_2CO_3 solution. The precipitated solid is made acid-insoluble by heating for several hours in a drying oven at 200°C; it is then freed of chlorides by vigorous boiling with dilute soda solution and distilled water. Finally, it is freed of alkali by treatment with dilute sulfuric acid and distilled water, filtered off and dried on a water bath.

PROPERTIES:

Straw yellow after brief drying; on further drying, becomes yellow ochre and then dark brown; at this point the oxide is acid-insoluble.

REFERENCE:

L. Wöhler, Z. anorg. Chem. 40, 436 (1904).

II. A 10% solution of H_2PtCl_6 (10 ml.) is added to 9 g. of $NaNO_3$ in a 50-ml. beaker. The solution is evaporated to dryness over a flame (covered with asbestos-wire gauze) while continuously stirring with a glass rod. Local melting of the mixture must be carefully avoided. Then 100 g. of $NaNO_3$ is heated to 520°C in a 400-ml. beaker (controlling the temperature with a thermocouple), and the dry, fine powder residue from the evaporation is added at once. The flame is then removed. The olive-brown platinum oxide is

precipitated more or less quantitatively and settles rapidly. During cooling and solidification, the beaker is rotated, so that the contents solidify on the walls in fine particles, thus avoiding the cracking of the beaker.

The cooled melt is dissolved in about two liters of H_2O, and the residue is filtered off with suction. It is then washed repeatedly with H_2O, taking care that the residue remains covered with water at all times, since otherwise it passes into solution as a colloid. Finally it is dried over $CaCl_2$ in an evacuated desiccator.

PROPERTIES:

Heavy brown powder; insoluble in aqua regia. Blackens and settles rapidly when treated with H_2 in an alcoholic suspension (this powder is soluble in aqua regia). Very active catalyst for the hydrogenation of olefins and carbonyl groups.

REFERENCE:

V. L. Framton, J. D. Edwards, Jr., and H. R. Henze, J. Amer. Chem. Soc. 73, 4432 (1951).

DropBooks

Hexahydroxyplatinates (IV)

$Na_2Pt(OH)_6 \cdot x H_2O$, $K_2Pt(OH)_6 \cdot x H_2O$

An aqueous solution of Na_2PtCl_6 or K_2PtCl_6 is boiled with NaOH and then treated with alcohol. The precipitate consists of small colorless crystals, which are filtered off and dried in air. Depending on the conditions of precipitation, the product contains from 0.5 to 3 moles of H_2O. Aqueous solutions of these two salts are very good electrolytes for electroplating platinum.

Platinum (II) Sulfide

PtS

Produced by heating an intimate mixture of very fine powders of platinum sponge and sulfur; may also be produced by decomposition of a boiling solution of $PtCl_2$ by bubbling in H_2S, or by adding to it a solution of one of the alkali sulfides. The black precipitate can be washed and dried without being altered.

PROPERTIES:

Insoluble in acids, even at the boil. Yields metallic Pt when heated in air.

Platinum (IV) Sulfide

PtS_2

Produced as a dark-brown precipitate by passing H_2S through a hot solution of H_2PtCl_6 in hydrochloric acid. The precipitation can be greatly accelerated and made almost quantitative if the weakly acidic platinate solution is mixed with a 5% solution of $MgCl_2$ and then saturated with H_2S gas. After the excess H_2S is driven off by boiling, the PtS_2 is filtered off and carefully dried.

PROPERTIES:

Insoluble in hydrochloric and sulfuric acids, soluble in nitric acid and particularly in aqua regia. Even though Pt belongs to the group of elements forming thio salts, PtS_2 is only slightly soluble in colorless alkali sulfides and yellow ammonium sulfide.

Potassium Tetracyanoplatinate (II) and Barium Tetracyanoplatinate (II)

$K_2Pt(CN)_4 \cdot 3\,H_2O$, $BaPt(CN)_4 \cdot 4\,H_2O$

Both salts are obtained by precipitation reactions.

$$\underset{268.0}{PtCl_2}\ \underset{(415.1)}{(K_2PtCl_4)} + 4\,KCN = \underset{431.4}{K_2Pt(CN)_4\,(3H_2O)} + 2\,KCl\ \underset{(298.2)}{(4\,KCl)}$$

$$\underset{431.4}{K_2Pt(CN)_4\,(3H_2O)} + \underset{244.3}{BaCl_2\,(2H_2O)} = \underset{526.6}{BaPt(CN)_4\,(5\,H_2O)} + \underset{149.1}{2\,KCl}$$

A solution of $PtCl_2$ or K_2PtCl_4 is added to a cold, saturated solution of KCN (use a good hood!). The precipitated $K_2Pt(CN)_4 \cdot 3\,H_2O$ is filtered off with suction. If it is to be used for preparing the barium salt, it is dissolved in water and treated with a concentrated aqueous solution of $BaCl_2$. The precipitated $BaPt(CN)_4 \cdot 4\,H_2O$ is filtered off with suction and washed with cold water.

SYNONYMS:

Potassium platinocyanide; barium platinocyanide.

PROPERTIES:

$K_2Pt(CN)_4 \cdot 3\,H_2O$: Polychromatic, blue and yellow. Readily soluble in hot water; most of it rapidly reprecipitates on cooling the solution. d 2.455.

$Ba[Pt(CN)_4] \cdot 4\,H_2O$: Crystals with brilliant polychromism (pleochroism), iridescent violet-blue on the prism faces, yellow-green in the axial direction. Solubility (20°C) 3.5 g./100 g. H_2O. d 2.076.

Ammine Complexes of Platinum (II)

(Platinum Ammines)

Magnus's Salt $[Pt(NH_3)_4][PtCl_4]$ and Reiset's First Chloride $[Pt(NH_3)_4]Cl_2 \cdot H_2O$

An excess of 50% ammonia is added to a boiling solution of H_2PtCl_4 (obtained by reduction of H_2PtCl_6, see p. 1570). Cooling precipitates the dark-green crystals of Magnus's salt. If heating with the excess of ammonia is continued with stirring, ignoring the appearance of the precipitate, the latter redissolves and the solution becomes colorless. It now contains $[Pt(NH_3)_4]Cl_2$, Reiset's first chloride. This salt can be precipitated directly by adding alcohol whereby it is obtained as colorless crystals. However, for higher purity, the preparation should proceed via Magnus's salt.

This requires a solution of H_2PtCl_4 in which the latter is present in a quantity exactly equivalent to the Reiset's chloride. The simplest way to achieve this is to divide a given quantity of H_2PtCl_4 solution into two equal parts and use only one of these for conversion of the solute to $[Pt(NH_3)_4]Cl_2$ in the manner described above. The excess NH_3 is driven off as completely as possible by heating on a water bath. The two solutions are then gradually combined (stirring), and pure green Magnus's salt is precipitated:

$$[Pt(NH_3)_4]Cl_2 + H_2PtCl_4 = [Pt(NH_3)_4][PtCl_4] + 2\,HCl$$

The precipitate is allowed to settle, the mother liquor decanted, and the solid washed with small portions of hot water (on a filter) until the wash water is free of chlorides. The Magnus's salt is now pure and can be dried.

For conversion into pure Reiset's chloride, the moist Magnus's salt is placed in a beaker, covered with some dil. hydrochloric acid, and treated with an excess of concentrated ammonia. The mixture is boiled gently with continuous stirring, gradually dissolving the solids. The evaporating ammonia must be replaced from time to time to maintain the original volume. After the green salt is completely dissolved the solution is evaporated until only a faint odor of NH_3 remains. Then it is neutralized to litmus, 1 ml. of concentrated HCl added, and the mixture treated with 10 times its volume of 1:1 alcohol-acetone. It is allowed to stand for an

hour; the white precipitate is removed, washed a few times with small portions of alcohol-acetone, and rinsed with pure acetone on a suction filter. The resulting Reiset's chloride is dried in air.

PROPERTIES:

Magnus's salt: Dark-green crystalline needles. Very difficult to dissolve in water. Rapidly transformed into trans-$[PtCl_2(NH_3)_2]$ on dry heating to 290°C.

Reiset's first chloride: Colorless tetragonal crystals. Solubility (20°C) about 20 g./100 g. H_2O; more soluble in hot water. Insoluble in alcohol, ether and acetone. Forms the hydrate $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ on recrystallization or concentration of an aqueous solution.

Reiset's Second Chloride

trans-$[PtCl_2(NH_3)_2]$

If Reiset's first chloride is heated at 250°C until no further NH_3 is given off, the product is trans-diamminedichloroplatinum (II):

$$\underset{334.1}{[Pt(NH_3)_4]Cl_2} = \underset{300.1}{[PtCl_2(NH_3)_2]} + \underset{34.1}{2\,NH_3}$$

A mixture of this chloride with NH_4Cl is obtained by evaporating the first chloride with a large excess of concentrated HCl; the NH_4Cl is extracted from the residue with cold water.

Purification is effected by recrystallization from hot water or by converting the solid to the nitrate by means of $AgNO_3$, followed by reprecipitation of the chloride from the nitrate solution with concentrated HCl.

PROPERTIES:

Sulfur-yellow crystalline powder. Very slightly soluble in cold water; solubility (100°C) 0.7 g./100 g. H_2O. Decomposes above 340°C.

Peyrone's Chloride

cis-$[PtCl_2(NH_3)_2]$

I. A cold, clear solution of 20 g. of $(NH_4)_2PtCl_4$ in 100 ml. of H_2O is reacted with 50 ml. of 5 N ammonia and allowed to stand for

12–48 hours in a closed flask at 0°C. The crystalline precipitate contains Peyrone's chloride and some Magnus's salt. The mixture is filtered off and washed with ice water until no Magnus's salt is precipitated from the filtrate with $PtCl_4^{2-}$. The Peyrone's chloride on the filter is then dissolved with boiling water, and the yellow solution is mixed with 1/3 its volume of 50% hydrochloric acid. After standing for 24 hours, the crystalline precipitate is filtered off, washed until free of acid with ice water and then with alcohol, and finally dried in air. Yield: 10.7 g.

II. A lukewarm solution of 41 g. of K_2PtCl_4 and 27 g. of NH_4Cl in 200 ml. of H_2O is reacted with 54.4 ml. of 3.75 N ammonia (0.204 mole) and allowed to stand for two days at room temperature and for an additional day at 0°C. The precipitate which has formed is then filtered off with suction (removing the liquid as completely as possible), thoroughly washed with ice water, and dried in air. The yield is 27.1 g. of a product which is not completely pure but contains, in addition to cis-$[PtCl_2(NH_3)_2]$, a few percent of Magnus's salt and $[PtCl(NH_3)_3]_2[PtCl_4]$.

PROPERTIES:

Yellow crystalline powder (needles or platelets). Solubility (0°C) 0.26 g., (100°C) 3 g./100 ml. H_2O. Dissolves very slowly in water at 100°C. Rapidly converted to the trans compound on dry heating to 275°C.

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REFERENCES:

Gmelins Handb. d. anorg. Chem. [Gmelin's Handbook of Inorganic Chemistry], 8th ed. (1957), Platinum, Part D, pp. 45, 53, 236, 241; S. M. Jörgensen. Z. anorg. Chem. 24, 153 (1900); S. M. Jörgensen and S. P. L. Jörgensen. Ibid. 48, 441 (1906); L. Ramberg. Ibid. 83, 33 (1913); R. N. Keller in: W. C. Fernelius, Inorg. Syntheses, Vol. II, New York-London, 1946, p. 250.

cis-Dinitrodiammineplatinum (II)

$[Pt(NO_2)_2(NH_3)_2]$

The cis form of this neutral salt complex is precipitated when an aqueous solution of potassium platinum (II) nitrite is treated with aqueous ammonia.

The starting $K_2Pt(NO_2)_4$ can be prepared from K_2PtCl_4 which is allowed to react with an excess of alkali nitrite, evolving nitric oxide.

$$\underset{486.0}{K_2PtCl_4} + 6\,\underset{414.0}{NaNO_2} = \underset{457.3}{K_2Pt(NO_2)_4} + 2\,NO + 6\,\underset{350.7}{NaCl}$$

One part by weight of K_2PtCl_6 is suspended in water and treated with a concentrated solution of 10 parts by weight of $NaNO_2$. The mixture is then heated with stirring. The yellow K_2PtCl_6 first dissolves giving a dark solution, and then nitric oxide is liberated as fine bubbles while the solution clears to a pale greenish yellow. When no further gas evolves the solution is cooled and, if necessary, the precipitated impurities are filtered off.

The $K_2Pt(NO_2)_4$ solution can also be prepared, in a smooth reaction, from K_2PtCl_4:

$$\underset{415.1}{K_2PtCl_4} + \underset{276.0}{4\,NaNO_2} = \underset{457.3}{K_2Pt(NO_2)_4} + \underset{233.8}{4\,NaCl}$$

To produce the desired complex $[Pt(NO_2)_2(NH_3)_2]$, the cold, filtered solution of $K_2Pt(NO_2)_4$ is reacted with a stoichiometric quantity of 20% aqueous ammonia:

$$\underset{457.4}{K_2Pt(NO_2)_4} + \underset{34.1}{2\,NH_3} = \underset{321.2}{[Pt(NO_2)_2(NH_3)_2]} + \underset{170.2}{2\,KNO_2}$$

After a short time the complex precipitates as a dense whitish mass of fine, needlelike crystals. After filtration and washing with cold water, it can be recrystallized from hot water; the product consists of pale-yellow needles.

PROPERTIES:

Formula weight 321.17. Pale-yellow needlelike crystals. Decompose explosively at 200°C. Sparingly soluble in water; readily soluble in aqueous ammonia, forming $[PtNO_2(NH_3)_3]NO_2$, which can be used to prepare a good platinum electroplating bath.

REFERENCE:

W. Keitel and H. E. Zschiegner. U.S. Patent 1,779,436.

Pure Palladium

Pd

In the Wilm method, very pure palladium is obtained by treating a solution of $PdCl_2$ or Na_2PdCl_4 with NH_4Cl in order to precipitate as $(NH_4)_2PtCl_6$ any slight Pt impurity which may be present. The filtrate is boiled with an excess of NH_3, filtered again if necessary, and acidified with HCl. A yellow precipitate of very pure $[PdCl_2(NH_3)_2]$ should form. If the salt has a dull, dirty yellow color,

it contains a small quantity of $[RhCl(NH_3)_5]Cl_2$, which is insoluble in cold ammonia. The salt is therefore digested with cold aqueous ammonia; completely pure palladodiammine chloride $[PdCl_2(NH_3)_2]$ is obtained from the filtrate by a second precipitation with hydrochloric acid; it is a bright-yellow crystalline salt. This is reduced by ignition in a stream of H_2 to light gray palladium sponge.

PROPERTIES:

M.p. 1554°C; d 11.97. Absorbs large quantities of many gases, especially H_2.

REFERENCE:

Th. Wilm. Ber. dtsch. chem. Ges. 15, 241 (1882).

Colloidal Palladium

A solution of 2 g. of sodium protalbinate (the sodium salt of protalbinic or lysalbinic acid) in 50 ml. of water is prepared; aqueous NaOH is added in slight excess, followed by a solution of 1.6 g of $PdCl_2$ (equivalent to 1 g. of Pd) in 25 ml. of H_2O. Then $N_2H_4 \cdot H_2O$ is added dropwise to the resulting clear red-brown liquid, producing immediate reduction (foaming). After standing for three hours, the black solution is dialyzed against water to remove the excess NaOH, $N_2H_4 \cdot H_2O$ and NaCl; this is continued until the dialyzing water no longer gives a reaction for $N_2H_4 \cdot H_2O$ and NaCl. The purified solution is concentrated at 60–70°C and dried in vacuum over H_2SO_4. The product consists of shiny black platelets, which dissolve in water leaving no residue.

PROPERTIES:

Stable when dry. Its solution appears opaque and black in incident light; thin layers are clear black-brown with a greenish tinge in transmitted light. One volume of the product (about 50% Pd) contained in this colloidal solution can absorb approximately 3000 volumes of H_2.

REFERENCES:

C. Paal and C. Amberger. Ber. dtsch. chem. Ges. 37, 124 (1904); P. Stecher et al. Merck Index, 7th ed., p. 623 under "lysalbinic acid."

Palladium Black

The Böttger method for preparing palladium black consists in reducing an aqueous solution of a Pd (II) salt with sodium formate:

The reaction occurs slowly at room temperature and is instantaneous at 50°C.

PROPERTIES:

According to C. Paal, an aqueous suspension of palladium black absorbs 12,000 times its volume of H_2; the dry material absorbs only 870 times its volume.

REFERENCE:

Jahresber. d. phys. Vereins Frankfurt a.M. [Annual Report of the Frankfurt a.M. Physics Society], 1872-73, p. 11.

Palladized Asbestos

Palladized asbestos is prepared in exactly the same way as platinized asbestos (see p. 1563).

Palladium (II) Cloride

$PdCl_2$

The anhydrous salt is prepared by heating loose palladium sponge (contained in a porcelain boat set in a glass tube) to a dull red heat in a stream of Cl_2. According to Krustinsons, the decomposition pressure of $PdCl_2$ reaches 1 atm. at 738°C.

By dissolving finely divided Pd in conc. HCl through which Cl_2 is bubbled, one obtains a solution in which both H_2PdCl_4 and H_2PdCl_6 can be detected. Concentrating the solution also yields a residue of $PdCl_2$.

$PdCl_2$ Solution for the Detection of CO

Winkler gives the following method for preparing this solution. Pure Pd (0.2 g.) is dissolved with gentle heating in about 10 ml. of aqua regia. The solution is evaporated to dryness in a 50-ml. porcelain dish placed on a steam bath. The residue is dissolved in 10 ml. of 20% hydrochloric acid and the solution is again evaporated to dryness; this last procedure is repeated three times. The resulting residue, which is now completely nitrate-free, is mixed with 2 g. of KBr and dissolved (gentle heating) in 10 ml. of 1 N HCl. After dilution to about 150 ml. with water, a few particles of pumice and 1 ml. of alcohol are added to the solution, which is then boiled for about 10 minutes in an Erlenmeyer flask in order

to reduce any Pd (IV) not decomposed during the drying to Pd (II) and to drive off the excess alcohol. After cooling, 2.5 g. of $CH_3COONa \cdot 3\ H_2O$ is dissolved in the liquid. The solution is filtered through a small wad of cotton wool and diluted to 200 ml. with the water used for washing the cotton wool. The clear, reddish-brown liquid, which contains 0.1% palladium, is stable when stored in a flask provided with a ground-glass stopper. To be on the safe side, it is best to filter the solution before use; it should be stored in the dark.

REFERENCES:

J. Krustinsons. Z. Elektrochem. 44, 537 (1938); L. Winkler. Z. anal. Chem. 100, 321 (1935); 97, 18 (1934); also describes analytical methods for detecting CO with $PdCl_2$ solutions. Explicit directions for the preparation of palladium catalysts using $PdCl_2$ are given by R. Mozingo in Organic Syntheses, collective vol. III, p. 685 (Wiley, New York, 1955).

Palladium (II) Oxide

PdO

DropBooks

A reasonably pure PdO, particularly suitable for catalytic purposes, can be prepared by decomposition of palladium nitrate. Sodium nitrate (50 g.) and a solution of $PdCl_2$ containing 2 g. of Pd are mixed and evaporated to dryness. The dry mixture is then heated (it fuses in the process), first for some time at 270–280°C, then at 350–370°C, until evolution of nitric oxides ceases; finally, it is heated to 575–600°C for a short time. The melt is extracted with 200 ml. of water, leaving behind the PdO. This is washed with a 1% $NaNO_3$ solution and dried in vacuum over H_2SO_4. The product still contains about 1.5% H_2O and 2.5% alkali salts. The pure material can be obtained by ignition in O_2, but this causes a loss of catalytic activity.

PROPERTIES:

Black powder; tetragonal crystals. Stable in air up to about 700°C, in O_2 to about 800°C. Insoluble in aqua regia; soluble in conc. HBr. d 8.7.

REFERENCES:

Gmelin, Handb. d. anorg. Chem. [Gmelin's Handbook of Inorganic Chemistry], 8th ed., System No. 65, Berlin, 1942; R. L. Shriner and R. Adams, J. Amer. Chem. Soc. 46, 1685 (1924).

Tetrachloropalladates (II)

K_2PdCl_4, Na_2PdCl_4, $(NH_4)_2PdCl_4$

$$PdCl_2 + 2\,KCl\ (2\,NaCl,\ 2\,NH_4Cl) = K_2PdCl_4\ [Na_2PdCl_4,\ (NH_4)_2PdCl_4]$$
$$177.3 \quad 149.1\ (116.9 \quad 107.0) \quad 328.4 \quad (294.2 \quad 284.3)$$

These three salts are obtained as well-formed crystals by treating $PdCl_2$ solutions with stoichiometric quantities of the respective alkali chlorides and slowly evaporating the solutions.

SYNONYMS:

Potassium, sodium and ammonium palladochlorides.

PROPERTIES:

K_2PdCl_4: Crystallizes in dark yellow or brownish prisms. Readily soluble in hot water, soluble with difficulty in cold water. Precipitated in golden yellow lamellae by addition of alcohol to a hot aqueous solution.

Na_2PdCl_4: Brown, deliquescent; also soluble in alcohol.

$(NH_4)_2PdCl_4$: Crystallizes in long olive-colored prisms; can be recrystallized from water.

Hexachloropalladates (IV)

K_2PdCl_6, $(NH_4)_2PdCl_6$

A solution of $PdCl_2$ with an excess of KCl (NH_4Cl) is prepared, from which bright red K_2PdCl_6 [$(NH_4)_2PdCl_6$] is precipitated on introduction of chlorine. This is rapidly suction-filtered, washed quickly with KCl (NH_4Cl)-containing water, and rinsed with alcohol.

SYNONYMS:

Potassium and ammonium palladium (IV) chlorides.

PROPERTIES:

Bright red crystals. Soluble with difficulty in water, even less soluble in KCl and NH_4Cl solutions. Crystal structure: K_2PtCl_6 type.

Diamminepalladium (II) Salts

$[PdCl_2(NH_3)_2]$, $[PdBr_2(NH_3)_2]$

If a slight excess of ammonia is added to a fairly dilute, cold solution of $PdCl_2$, a red precipitate known as Vauquelin's salt is formed. After drying, this becomes a crystalline, flesh-colored to dark-red powder, corresponding to the formula $[Pd(NH_3)_4][PdCl_4]$ (analogous to Magnus's green platinum salt). On boiling in water, most of it dissolves; the solution precipitates small yellow octahedral crystals on cooling; this is trans-$[PdCl_2(NH_3)_2]$. Larger quantities can be easily prepared via methods described in the section on the preparation of pure palladium (p. 1580).

A $PdBr_2$ solution behaves in an exactly parallel manner upon addition of ammonia: a red, crystalline precipitate of $[Pd(NH_3)_4][PdBr_4]$ is obtained from the mixture. This undergoes the same transformation as the chloride to give yellow octahedral crystals of $[PdBr_2(NH_3)_2]$.

Pure Rhodium

Rh

DropBooks

I. Reasonably pure sodium or potassium hexachlororhodate (see p. 1588 for preparation) is the starting material. The salt is dissolved in water; the solution is boiled with an excess of ammonia and concentrated. This gives the so called purpureo salt $[RhCl(NH_3)_5]Cl_2$ as a straw-colored powder, which must be purified. The salt is first digested for a long time in hot 50% hydrochloric acid, is then suction filtered (removing as much water as possible) and dried. The lumps are carefully broken up with a broad glass spatula and transferred to a container of cold, concentrated H_2SO_4 (salt: H_2SO_4 ratio = 1 : 1.5). Too large an excess of H_2SO_4 should be avoided, and the mixture should be warmed very carefully, since otherwise an insoluble sulfate will result. Upon addition of the powder, small lumps, not wetted by the H_2SO_4, are easily formed; these must be broken up with the glass spatula. The powder must be added in small portions with continuous stirring; the HCl escapes in bubbles, so that the mass foams. It is digested until it becomes a honeylike, viscous, lump-free yellowish paste. Hot water is added and the mass is filtered; the filtrate is allowed to run into concentrated HCl so that the resulting solution is approximately 50% in hydrochloric acid. The purified purpureo salt precipitates as a dense, yellowish-white residue. It is filtered off with suction, washed, dried, ground with a glass spatula, and boiled

for two hours with five times its quantity of concentrated HNO_3, after which the solution is mixed with an equal volume of water. The nitrate is allowed to crystallize overnight; it is then filtered off, washed and recrystallized once from water. It is then redissolved in water, the solution is filtered, and the filtrate is again allowed to run into hydrochloric acid. The salt is washed with liquids whose compositions approximate those of the respective mother liquors. Since the salt is only slightly soluble in cold H_2O, it is given a final rapid wash with cold H_2O, preferably on a filter connected to a vacuum pump. The purpureochloride obtained in this way is placed in a covered quartz crucible set inside a graphite crucible and ignited carefully in a gas-heated or muffle furnace.

II. According to Wichers and Gilchrist, pure rhodium can be prepared as follows. The finely divided, impure metallic raw material is mixed intimately with 1.5 times its weight of NaCl and heated at 600°C in a stream of Cl_2 for 2-4 hours. It is then cooled in the stream of Cl_2, and the fused mass is dissolved in H_2O. The insoluble residue is again treated with chlorine until all of the rhodium becomes soluble. The solution is then diluted to a concentration of 40 g. of Rh/liter and filtered. The filtrate is heated on a steam bath and $NaNO_2$ is added until the color changes from red to yellow; this requires about 500-550 g. of $NaNO_2$ per 100 g. of Rh. Finally the solution is boiled for an hour. The platinum metals and some of the base metals are converted into soluble double nitrites, while other base metals are precipitated as hydroxides or basic salts. The mixture is filtered; the cold solution is treated with Na_2S and allowed to stand overnight (5-10 g. of Na_2S is sufficient for a solution containing several hundred g. of Rh). The odor of H_2S indicates the end of the reaction, which precipitates Pb and small quantities of Pd, Pt and Ir. The filtrate is boiled to decompose the excess Na_2S. The purified solution is again treated with 30-50 g. of $NaNO_2$ per 100 g. of Rh (to convert the rhodium completely to the double nitrite). The cooled solution is treated with a saturated solution of NH_4Cl, which precipitates the sparingly soluble $(NH_4)_3[Rh(NO_2)_6]$, which is white when pure. This product is allowed to react with hydrochloric acid. The resulting hydrochloric acid solution of rhodium chloride is treated with $NaNO_2$ (after evaporating the excess of the acid) and treated again as described above, except that smaller additions of Na_2S are made in the successive purifications. Finally, the concentrated solution of rhodium chloride in hydrochloric acid is converted to $(NH_4)_3RhCl_6 \cdot H_2O$ by addition of a small excess of NH_4Cl, and the mixture is treated with 95% alcohol. The precipitate is filtered off and washed with alcohol. The $(NH_4)_3RhCl_6 \cdot H_2O$ may be redissolved in water and reprecipitated with alcohol.

The $(NH_4)_3RhCl_6 \cdot H_2O$ is ignited to rhodium sponge and post-reduced with hydrogen.

PROPERTIES:

M.p. 1970°C. Harder and more difficult to work than Pt. The solid metal and the fine rhodium black powder obtained by reduction from salt solutions differ in their solubility in acids. The solid metal is insoluble in all acids and mixtures of acids, and is not attacked by molten NaOH even if KNO_3 is added at dull red heat. If Rh is fused with $KHSO_4$, it slowly forms the water-soluble potassium rhodium sulfate, which imparts a dark-red color to the melt; at high Rh concentrations, the melt becomes black.

REFERENCE:

E. Wichers and R. Gilchrist, Trans. Amer. Inst. Mining Metallurg. Eng. 76, 619 (1928).

Rhodium (III) Chloride

$RhCl_3$

DropBooks

The anhydrous chloride is prepared by heating the metal in a stream of Cl_2 at about 400°C. Above 800°C, it redecomposes to the metal and chlorine. This chloride is red and insoluble in water and acids.

However, the hydrated rhodium (III) oxide mentioned on page 1588 dissolves readily in hydrochloric acid, giving a yellow solution. On evaporation of this solution, a residue of the hydrated chloride $RhCl_3 \cdot xH_2O$ (x = 3–4) is left as a red deliquescent mass, which is called "water-soluble rhodium chloride" to distinguish it from the first product. Heating above 200°C converts this product to the water-insoluble $RhCl_3$.

Hexachlororhodates (III)

Sodium hexachlororhodate (III), $Na_3RhCl_6 \cdot 12\,H_2O$

First $RhCl_3$ is prepared by passing Cl_2 over very fine rhodium powder at about 400°C. One part by weight of the product $RhCl_3$ is carefully mixed with 2–3 parts by weight of NaCl and heated to about 300°C in a stream of Cl_2. The aqueous solution of this chlorination product is filtered; after concentration, $Na_3RhCl_6 \cdot 12\,H_2O$ crystallizes out as deep-red, monoclinic prismatic crystals.

Potassium hexachlororhodate (III), $K_3RhCl_6 \cdot H_2O$, $K_2[RhCl_5(H_2O)]$

A solution of the potassium salt is prepared in exactly the same way as that of the sodium salt. On concentration, the first crystallization yields $K_2[RhCl_5(H_2O)]$. This salt is dissolved in an almost saturated aqueous KCl solution and the solution concentrated; the hexachlororhodate $K_3RhCl_6 \cdot H_2O$ crystallizes out on cooling. Both of the above compounds form dark-red crystals.

Ammonium hexachlororhodate (III), $(NH_4)_3RhCl_6 \cdot H_2O$, $(NH_4)_2[RhCl_5(H_2O)]$

Concentration of a platinum-rhodium solution which has been freed of platinum by the addition of NH_4Cl yields crystals of the red $(NH_4)_3RhCl_6 \cdot H_2O$. Green crystals occasionally obtained are $(NH_4)_2PtCl_6$ containing Rh as an impurity.

A better method starts with soluble rhodium chloride (see page 1587), which is evaporated together with an excess of aqueous NH_4Cl.

If the $(NH_4)_3RhCl_6 \cdot H_2O$ is taken up in water and heated to a high temperature, the much less soluble $(NH_4)_2[RhCl_5(H_2O)]$ crystallizes out on cooling.

REFERENCE:

M. Delépine. Bull. Soc. Chim. Belgique 36, 114 (1927).

Rhodium (III) Oxide

Rh_2O_3

I. Very pure Rh_2O_3 is obtained by heating $RhCl_3$ to 750-800°C in a stream of O_2 until Cl_2 is no longer given off.

II. The highly hydrated compound $Rh_2O_3 \cdot 5\ H_2O$ is obtained when concentrated KOH is added slowly to solutions of rhodium salts. A lemon-yellow compound precipitates; after washing and drying, it becomes a pale-yellow powder. This material is not completely alkali-free and is insoluble in water; however, it dissolves readily in acids and on ignition reverts to nonhydrated Rh_2O_3, which is insoluble in acids.

SYNONYM:

$Rh_2O_3 \cdot 5\ H_2O$: Rhodium hydroxide.

REFERENCES:

I. Gmelin. Handb. d. anorg. Chem. [Gmelin's Handbook of Inorganic Chemistry], 8th ed., Rhodium, p. 46; L. Wöhler and W. Müller. Z. anorg. allg. Chem. 149, 132 (1925).
II. F. Krauss and H. Umbach. Z. anorg. allg. Chem. 180, 47 (1929); G. Grube and G. Bau-Tschang Gu. Z. Elektrochem. 43, 398 (1937).

Rhodium Sulfate

$Rh_2(SO_4)_3 \cdot x\,H_2O$

According to Krauss and Umbach, attempts to prepare rhodium sulfate from rhodium hydroxide and sulfuric acid lead to two different products, depending on the conditions: these are yellow rhodium sulfate $Rh_2(SO_4)_3 \cdot 15\,H_2O$ and red rhodium sulfate $Rh_2(SO_4)_3 \cdot 4\,H_2O$.

$Rh_2(SO_4)_3 \cdot 15\,H_2O$

The yellow sulfate is produced on solution of moist hydrated rhodium (III) oxide (rhodium hydroxide) in dilute (1:10) sulfuric acid at temperatures not exceeding 50°C. Then the hydrated Rh (III) oxide is precipitated from the cold solution with KOH (avoiding an excess of the latter) and washed on a membrane filter until the colloidal hydroxide passes through. Suction is then applied and as much water as possible is removed; the residue is dissolved without heating in dilute sulfuric acid.

The solid salt is obtained by evaporating this solution in vacuum, dissolving the residue in absolute alcohol, and precipitating with 10–20 times its volume of ether; this gives a pale-yellow, fine, flocculent residue. After filtration, washing and drying, this becomes a light, yellowish-white powder. The yield is always poor, at most 20%.

$Rh_2(SO_4)_3 \cdot 4\,H_2O$

Red, amorphous rhodium sulfate is obtained either by evaporating a solution of the isomeric yellow salt or by precipitating hydrated Rh (III) oxide from a $RhCl_3$ solution at the boiling point, washing the precipitate with hot water, dissolving it in hot dilute sulfuric acid, and evaporating the mixture. To remove the excess H_2SO_4, the product is dissolved in H_2O and $Ba(OH)_2$ is added until Rh (III) hydroxide begins to precipitate. The solution is filtered and again evaporated.

The two sulfates undergo quite different precipitation reactions. Barium chloride precipitates the SO_4^{2-} almost quantitatively from solutions of the yellow salt prepared in the cold. These are acidic and KOH precipitates the rhodium from such solutions. On the other hand, the red salt solutions prepared under the same conditions either fail to give these reactions, or react only gradually, but in any case, not quantitatively. We must therefore conclude that in this last case we are dealing with a complex in which the bonds are stronger than in the yellow salt.

REFERENCE:

F. Krauss and H. Umbach. Z. anorg. allg. Chem. 180, 42 (1929).

Chloropentaammine rhodium Salts

$[RhCl(NH_3)_5]Cl_2$, $[RhCl(NH_3)_5](NO_3)_2$

The preparation of the chloride and nitrate of these compounds, which are also known as purpureo salts, is given in the section on the preparation of pure rhodium (p. 1585 ff.).

Pure Iridium

Ir

Chemically pure iridium is best prepared by ignition of $(NH_4)_2IrCl_6$. To obtain especially pure material, the metal should be reconverted to $(NH_4)_2IrCl_6$ (see p. 1594), which is then re-ignited.

PROPERTIES:

Very hard, fairly brittle metal; m.p. 2454°C. On ignition in air, forms small quantities of a volatile unstable oxide, IrO_3; thus, under conditions of oxidizing ignition the weight of Pt-Ir alloys does not remain constant. Extraordinarily resistant to acids; insoluble even in aqua regia. Attacked with comparative ease by Cl_2, particularly in the presence of NaCl, with which the nascent chloride forms a double salt.

Iridium (IV) Oxide

IrO_2

In the method of Wöhler and Streicher, IrO_2 is prepared from green $IrCl_3$ which can be readily oxidized in a stream of O_2 at 800°C, giving blue-black IrO_2.

The oxidation of fine iridium powder in a stream of air or oxygen does not give IrO_2 quantitatively.

PROPERTIES:

Black to blue-black powder, insoluble in acids. Crystal structure: rutile type.

REFERENCE:

L. Wöhler and S. Streicher. Ber. dtsch. chem. Ges. 46, 1721 (1913).

Hydrated Iridium (IV) Oxide

$IrO_2 \cdot 2H_2O$

I. An aqueous solution of $IrCl_4$ or H_2IrCl_6, prepared by the old method of Vauquelin (see H_2IrCl_6, method I, p. 1593), is evaporated several times to a sirupy consistency in a vacuum at 40 °C. After each evaporation, the sirup is redissolved in water; this treatment completely removes the excess of HCl. The final concentrate is again diluted, and dilute aqueous KOH is added in drops to the boiling solution until the color changes from dark red-brown to green and then to blue. The solution is then held at the b.p. for some time to oxidize any Ir (III) which may be present and to complete the precipitation of the hydrated Ir (IV) oxide. The residue of deep-blue coarse floc is filtered off, washed with water, then with absolute alcohol, and dried in a vacuum desiccator.

II. Gerlach's method consists in adding the KOH solution in drops to a boiling solution of Na_2IrCl_6, to give the alkali-free hydrated oxide. The use of excess hydroxide leads to a product which contains alkali. Purification is the same as in method I.

PROPERTIES:

Very dark-blue powder. The hydrated oxide prepared by method I may be converted to IrO_2 at 350 °C in a stream of N_2. Freshly precipitated $IrO_2 \cdot 2H_2O$ is soluble in acids.

REFERENCES:

I. F. Krauss and H. Gerlach. Z. anorg. allg. Chem. 143, 126 (1925).
II. H. Gerlach. Thesis, Tech. Hochschule, Braunschweig, 1925, pp. 4, 42; N. K. Pschenizyn and S. E. Krassikow, abstract in Chem. Zentr. 1933, I, 3911.

PrepBooks

Hydrated Iridium (III) Oxide

$Ir_2O_3 \cdot x\,H_2O$

A solution of Na_3IrCl_6 is prepared either in the same way as in method II for $K_3IrCl_6 \cdot 3\,H_2O$ (see p. 1594) or, better, as suggested by Ogawa, from a solution of Na_2IrCl_6 and sodium oxalate at 50°C according to the equation

$$2\,Na_2[IrCl_6] + Na_2C_2O_4 = 2\,Na_3[IrCl_6] + 2\,CO_2$$

In either case the solution is treated with potassium hydroxide or potassium carbonate solution in a stream of CO_2. The separation, washing and drying of the hydrated oxide must be carried out under an inert gas (CO_2 or N_2). The alkali cannot be completely removed from the product.

PROPERTIES:

Pale-green to dark powder, depending on the precipitation conditions and water content; oxidized in air to the hydrated Ir (IV) oxide, particularly when damp. The Ir (III) compounds are more stable in acid solutions than the Ir (IV) salts; the reverse is true in alkaline solutions.

REFERENCES:

L. Wöhler and W. Witzmann, Z. anorg. Chem. 57, 334 (1908); Preparation of Na_3IrCl_6 solution: E. Ogawa, J. Chem. Soc. Japan 50, 246 (1929).

Iridium (III) Chloride

$IrCl_3$

L

$$\underset{192.2}{Ir} + 1\tfrac{1}{2}\,\underset{106.4}{Cl_2} = \underset{298.6}{IrCl_3}$$

Fine iridium powder is placed in a porcelain boat set in an open-end glass combustion tube. The gas inlet side of the tube is drawn to a small-diameter tubing, while the other end carries a ground-glass joint. An O_2-free stream of chlorine, containing a small percentage of CO, is passed through the tube, which is heated to about 600°C with a burner and illuminated either with direct sunlight or light from a burning magnesium ribbon. The chlorination is complete in about 15 minutes.

II. Alternatively, $IrO_2 \cdot 2\,H_2O$ is heated to 240°C in a stream of Cl_2 and illuminated with sunlight or a burning magnesium ribbon.

III. Finally, $(NH_4)_2IrCl_6$ may be decomposed in a stream of Cl_2 at 440–550°C; the conversion of 0.5 g. requires two hours.

PROPERTIES:

Dark olive-green powder. Stable up to 760°C under a Cl_2 pressure of 1 atm. (Streicher); at 700°C the color changes to bright yellow.

REFERENCES:

F. Krauss and H. Gerlach. Z. anorg. allg. Chem. 147, 265 (1925); L. Wöhler and S. Streicher. Ber. dtsch. chem. Ges. 46, 1720, 1582 (1913); S. Streicher. Thesis, Univ. of Darmstadt, 1913.

Hexachloroiridic (IV) Acid

H_2IrCl_6

I. A solution of $(NH_4)_2IrCl_6$ is decomposed by bubbling Cl_2 through it at about 4°C; then the liquid is concentrated at 40°C (12–15 mm.) until a dark-brown sirupy mass results. This is allowed to stand for some time in an evacuated desiccator containing CaO (until it congeals and crystallizes). The low temperatures mentioned must be maintained to avoid the formation of NCl_3.

II. A solution of $(NH_4)_2IrCl_6$ is heated with aqua regia on a water bath (approximately 10 hours) until the NH_4^+ is completely split off; the solution is repeatedly concentrated with conc. HCl until the HNO_3 is completely removed.

REFERENCES:

I. Vauquelin. Liebigs Ann. 89, 150, 225 (1845); A. Gutbier and F. Lindner. Z. phys. Chem. 69, 304 (1909).
II. S. C. Woo and D. M. Yost. J. Amer. Chem. Soc. 53, 884 (1931).

Potassium Hexachloroiridate (IV)

K_2IrCl_6

I. A mixture of fine iridium powder and twice its weight of KCl is heated in a porcelain boat almost to red heat while chlorine is

passed over it. After cooling, the excess KCl is extracted by washing with the least possible quantity of cold water. Then the double salt is dissolved in boiling water and filtered free of unconverted Ir. The solution is slowly evaporated in a porcelain dish. The K_2IrCl_6 crystallizes as small, shiny, red-black octahedra, which yield a red powder on grinding.

In the above extraction with boiling water it is best to add a few drops of nitric acid in order to prevent the formation of K_3IrCl_6 and convert any Ir (III) present to Ir (IV).

II. According to Puche, better results are obtained by allowing Na_2IrCl_6 solution to react with solid KCl while a stream of Cl_2 is bubbled through the mixture. The crystalline deposit is filtered off with suction and washed several times with dilute alcohol. It is then rapidly washed with some water. The product is dried in a drying oven at about 100°C.

PROPERTIES:

Deep dark-red octahedra. Solubility (20°C) 1.12 g./100 g. H_2O. Insoluble in alcohol. d 3.5.

REFERENCES:

I. Old process of Berzelius: G. Gire. Ann. Chim. 4, 210 (1925).
II. F. Puche. Ibid. 9, 270 (1938).

Ammonium Hexachloroiridate (IV)

$(NH_4)_2IrCl_6$

A mixture of iridium metal powder plus twice its weight of NaCl is converted to Na_2IrCl_6 by heating to 400°C in a stream of Cl_2 (compare the preparation of the analogous K_2IrCl_6); this salt is dissolved in some water. Addition of NH_4Cl to this solution [or to other solutions of Ir (IV)] leads to the formation of $(NH_4)_2IrCl_6$; the latter is only slightly soluble.

SYNONYM:

Ammonium iridium (IV) chloride.

PROPERTIES:

Dark-red octahedra. Solubility (cold) about 5 g., (100°C) about 10 g./100 ml. H_2O. d 3.03. Crystal structure: K_2PtCl_6 type.

REFERENCE:

A. Gutbier. Z. phys. Chem. 69, 307 (1909).

Potassium Hexachloroiridate (III)

$K_3IrCl_6 \cdot 3H_2O$

I. A hydrogen stream is passed over gently heated (not over 150°C) K_2IrCl_6 placed in a quartz or porcelain boat; the reduction proceeds according to the equation

$$3K_2IrCl_6 + 3H_2 = 2K_3IrCl_6 + Ir + 6HCl$$

II. A solution of K_2IrCl_6 (the concentration should be as high as possible) in freshly prepared H_2S water is heated until the color turns olive-green. Then KCl is added and crystals of $K_3IrCl_6 \cdot 3H_2O$ deposit out; these can be dehydrated, if need be. The K_2IrCl_6 can be reduced with SO_2 in the same manner, but the product must be neutralized with K_2CO_3.

Alternate method: Reduction with oxalate: see section on $Ir_2O_3 \cdot xH_2O$ (p. 1592).

SYNONYM:

Potassium iridium (III) chloride.

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PROPERTIES:

Dark olive-green crystals. Readily soluble in water, insoluble in alcohol.

REFERENCE:

I. F. Puche, Ann. Chim. 9, 273 (1938).

Pure Ruthenium

Ru

Gutbier and Trenkner give the following method for the preparation of the pure metal. To start with, 30 g. of the fine metal powder is heated to dull red heat for three hours in a stream of O_2 in order to volatilize Os, which is often present as an impurity. The partially oxidized Ru is then reduced in a stream of H_2; then a mixture of the metal, the purest KOH, and the purest KNO_3 (3 : 25 : 3 by weight) is prepared and fused in a flat silver dish.

The green melt is kept in the liquid state for half an hour. It is then cooled, and the reaction product is broken into small lumps and dissolved in lukewarm water. The orange-yellow solution is poured into a large retort, the neck of which is joined to a 2-m.-long glass tube in such a way that the neck of the retort projects as far as possible into the tube. That tube is placed in a metal trough of about the same length filled with an ice-salt mixture. The other end of the tube is connected to a flask half-filled with 30% KOH. Then a fast stream of dry Cl_2 is introduced through the filler tube of the retort. So much heat of reaction is evolved that the RuO_4 distills over in a very short time. It is in the form of golden-yellow drops which solidify as a yellowish-red mass in the cooled condenser tube.

As soon as the formation of the tetroxide subsides, the contents of the retort are heated to 80-90°C with a microburner while continuing to introduce Cl_2; the whole operation is stopped only when a yellow vapor (a mixture of RuO_4 and Cl_2) can be seen in the attached flask. Since only ruthenium is capable of forming volatile compounds under these conditions (the osmium having been removed previously), all the other impurities remain in the retort.

To convert the tetroxide to the metal, the RuO_4 is washed out from the tube with lukewarm water, transferred to a porcelain dish and, when completely dissolved, reduced immediately with pure alcohol (if the alcohol is added before solution is complete a violent explosion may occur!). The resulting inky liquid is concentrated on a water bath and the residue reduced to elemental Ru with pure H_2.

Alternate method: A method which is related to the analytical procedure of Wichers et al. separates the osmium by distillation of a nitric acid solution of the products of the alkali fusion step. The residue from this distillation is made alkaline and ruthenium is then distilled off, using Cl_2 as above. Regarding the danger of explosions, see the properties of RuO_4.

PROPERTIES:

M. p. ~ 2400°C; d 12.43. Very hard and brittle; can be pulverized. When melted, part of the metal oxidizes and volatilizes as RuO_4, which is stable at very high temperatures and gives off a peculiar choking odor.

REFERENCES:

A. Gutbier and C. Trenkner. Z. anorg. Chem. 54, 167 (1905); E. Wichers, R. Gilchrist and W. H. Swanger. Trans. Amer. Inst. Mining Metallurg. Eng. 76, 626 (1928).

Ruthenium (IV) Hydroxychloride

$Ru(OH)Cl_3$

Heating of RuO_4 with conc. HCl on a water bath gives a dark-brown solution; according to Remy and Wagner, this contains the Ru (IV) chloride. If inhibited, the reaction (which involves the splitting off of Cl_2) can be started by addition of a few drops of alcohol. The product solution is evaporated and a dark-brown product [$Ru(OH)Cl_3$] is obtained. On the basis of an early incorrect assumption, this is often called "water-soluble ruthenium trichloride."

PROPERTIES:

Dark-brown salt. Very readily soluble in water. A certain proportion is apparently always present as $RuCl_3$.

REFERENCES:

A. Gutbier and C. Trenkner. Z. anorg. Chem. 45, 167 (1905). H. Remy and A. Lührs. Ber. dtsch. chem. Ges. 61, 917 (1928); 62, 201 (1929); H. Remy. Ibid. 61, 2110 (1928).

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Ruthenium (III) Chloride

$RuCl_3$, $RuCl_3 \cdot H_2O$

$RuCl_3$

I. In the method of Remy et al., a mixture of carefully predried Cl_2 and CO (initial ratio of 1:4) is passed over a boat containing ruthenium powder and placed in a Vycor combustion tube. After displacing all the air from the tube, the latter is heated to 700-800°C, and the fraction of Cl_2 in the gas stream is simultaneously increased. The beginning of the reaction is clearly marked by a considerable swelling of the material. At the end of the reaction the boat is kept for half an hour at bright red heat, and the CO throughput is gradually reduced and finally stopped. Cooling in the Cl_2 stream yields a well-crystallized product.

II. In the method of Wöhler and Balz, $RuCl_3$ is prepared without the use of CO. A mixture of the metal and NaCl is heated at 700°C in a stream of Cl_2, after which the products are reduced with H_2 at 400°C and extracted with H_2O. The finely divided, velvety-black metal obtained in this way is chlorinated at 800°C.

PROPERTIES:

Formula weight 207.5. Method I gives good crystals in the form of shiny black platelets. Insoluble in water.

REFERENCES:

I. H. Remy (with M. Köhn). Z. anorg. allg. Chem. 137, 365 (1924); H. Remy and Th. Wagner. Ibid. 168, 2 (1928).
II. L. Wöhler and P. Balz. Ibid. 139, 413 (1924).

$RuCl_3 \cdot H_2O$

Since warm hydrochloric acid solutions of Ru (III) are partly oxidized by atmospheric oxygen (for example, on concentration) commercial "water-soluble ruthenium trichloride" is not free of Ru (IV). A pure product corresponding to the formula $RuCl_3 \cdot H_2O$ can be obtained from this material by electrolytic reduction.

A cathode of platinized Pt foil (40 × 35 mm.) and an anode of polished Pt foil are suspended inside a small porous clay cylinder placed inside a rectangular, 200-ml. glass trough. The cathode liquid is a 0.03 M solution of commercial $RuCl_3$ [or a solution of an evaporation residue which corresponds approximately to $Ru(OH)Cl_3$] which is 2N in HCl; the anode liquid is 2N HCl. Efficient stirring is necessary. The electrolysis is carried out at 0.03–0.1 amp., with separate control of the cathode potential. The initial dark-brown color of the solution gradually clears. The electrolysis is stopped when the cathode potential becomes constant at 0.01 volt and H_2 evolution commences. The reduced solution should be red. A blue color indicates the formation of the undesirable Ru (II).

The $RuCl_3$ solution must be concentrated to crystallization in the absence of air, in order to prevent reoxidation by atmospheric oxygen. The evaporation is carried out in a round-bottom flask fitted with a dropping funnel; the flask is purged of air with HCl gas. The reduced solution is then introduced via the dropping funnel; with HCl continuously passing over it, it is evaporated at the boiling point to a sirupy thickness, and finally to dryness at 80–100°C. It is finally dried to constant weight in a vacuum desiccator over H_2SO_4.

The salt obtained in this way is free of Ru (IV) and has the composition indicated by the formula.

REFERENCE:

G. Grube and G. Fromm. Z. Elektrochem. 46, 661 (1940).

Ammonium Hexachlororuthenate (IV)

$(NH_4)_2RuCl_6$

A concentrated solution of NH_4Cl is added to a ruthenium chloride solution and the resultant mixture concentrated in air. The dark-red crystalline powder is not homogeneous: it contains $(NH_4)_2[Ru(OH)Cl_5]$.

SYNONYM:

Ammonium ruthenium (IV) chloride.

Ruthenium (IV) Oxide

RuO_2

In the method of Remy and Köhn, RuO_2 is prepared by heating fine ruthenium powder at about 1000°C in a stream of carefully predried O_2. It can also be prepared by ignition of RuS_2 in air (the RuS_2 is obtained by precipitation of ruthenium chloride solutions with H_2S). Wöhler et al. suggest heating pure $RuCl_3$ at 600–700°C in a stream of O_2.

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PROPERTIES:

Dark-gray powder with a metallic luster, irideaces green and blue. Insoluble in acids. Readily reduced by H_2 even at moderate heating. d 7.0. Crystal structure: rutile type.

REFERENCES:

H. Remy (with M. Köhn). Z. anorg. allg. Chem. 137, 381 (1924); L. Wöhler, P. Balz and L. Metz. Ibid. 139, 213 (1924).

Ruthenium (VIII) Oxide

RuO_4

Chlorine is passed through a solution of an alkali ruthenate, as described earlier in the section on the purification of ruthenium.

In another method (Ruff and Vidic) mixtures of ruthenium powder with $KMnO_4$ and KOH are fused; the ruthenate produced in this way is decomposed with H_2SO_4 while still hot; a CO_2 stream is simultaneously passed through the reaction vessel and the RuO_4 distills off.

A mixture of Ru, $KMnO_4$ and KOH (1 : 2 : 20 by weight) is fused to a mobile liquid. The dark-green melt is kept liquid for 0.5–1 hour after all the permanganate has been added. After cooling, the melt is dissolved in water and placed, with one additional part of $KMnO_4$, in a flask fitted with a dropping funnel and containing 1 : 3 H_2SO_4. An ice-cooled flask containing some water is used as the first receiver (no alcohol! see properties), followed by a flask containing some 7% NaOH. Sulfuric acid is introduced until the color changes from green to red; then further H_2SO_4 (1/3 of the total liquid volume) is added. After this a fast air stream is bubbled through while the solution is heated to 40–50°C. Long golden-yellow needles of RuO_4 soon form in the ice-cooled flask. Later, ruthenate is formed in the NaOH solution, producing an orange-red color. Finally the solution is heated to boiling in order to steam-distill any remaining RuO_4. The yield is almost quantitative.

PROPERTIES:

Formula weight 497.1. A solid composed of golden-yellow rhombic prisms. Very volatile, subliming even at room temperature. Characteristic odor comparable to nitric oxide or ozone; very irritating to the respiratory tract. Less irritating to the eyes than OsO_4. Melts at 25°C to an orange-red liquid. Solubility (20°C): 20.3 g./liter of H_2O. Vapors and concentrated solutions tend to react explosively with organic substances, such as alcohol, filter fibers, etc. Distillation must therefore be carried out in perfectly clean equipment.

REFERENCE:

O. R. Ruff and E. Vidic. Z. anorg. allg. Chem. 136, 49 (1924).

Potassium Ruthenate and Potassium Perruthenate

$K_2RuO_4 \cdot H_2O$, $KRuO_4$

A dark-green melt is obtained by heating a mixture of Ru powder with KOH and adding $KClO_3$ or KNO_3; this readily takes up water, giving an orange-red solution. On evaporation, $K_2RuO_4 \cdot H_2O$ crystallizes in iridescent green prisms which appear red when spread in thin layers and viewed by transmitted light. If Cl_2 is introduced into the red solution, the latter becomes green due to the formation of perruthenate. Continued passage of Cl_2 yields RuO_4. However, if the Cl_2 stream is shut off at the right moment, $KRuO_4$ is precipitated on cooling as small black tetragonal crystals. In contrast to the ruthenates, the perruthenates are not stable above 200°C.

REFERENCES:

A. Gutbier, F. Falco and H. Zwicker. Z. anorg. Chem. 22, 490 (1909); F. Krauss. Z. anorg. allg. Chem. 132, 306 (1924).

Pure Osmium

Os

Osmium powder is purified by fusion in an oxidizing alkali melt. Nitric acid liberates the volatile OsO_4 from an aqueous solution of this melt; the OsO_4 is distilled in a stream of air into a receiver containing aqueous NaOH and is absorbed. The osmium is then re-precipitated as OsS_2 and filtered off. It is reduced to the metal in a stream of hydrogen.

The procedure is almost the same as in the purification of ruthenium. The fine metal powder is mixed with KOH and KNO_3 and fused at red heat. After cooling, the melt is dissolved in water in a retort. Nitric acid is added until the solution becomes acidic, and the OsO_4 liberated is carried in an air or oxygen stream to a receiver containing aqueous NaOH, in which it is absorbed. The solution is treated with H_2S, which precipitates the osmium quantitatively (as OsS_2). The precipitate is filtered off and reduced in a stream of hydrogen.

Since the sulfur is difficult to extract from the metal after the hydrogen reduction, the distillation receiver can also be charged with aqueous KOH (instead of NaOH), the resulting osmic acid salt may be reduced to K_2OsO_4 with alcohol, and the K_2OsO_4 reduced to Os with H_2.

PROPERTIES:

M.p. > 3000°C. Very hard and brittle, readily pulverized. The powder always retains the characteristic odor of OsO_4, since traces of the latter are formed in air even at room temperatures. Heating in air leads to complete combustion to OsO_4.

Osmium (IV) Chloride

$OsCl_4$

$$Os + 2\,Cl_2 = OsCl_4$$
$$190.2 \quad 141.8 \quad 332.1$$

Small quantities of Os (prepared, for instance, by reduction of OsO_2 with H_2) are heated to 650–700°C in a porcelain boat set in

a glass combustion tube, while a slow stream of very pure Cl_2 is passed through. The tube is constricted beyond the boat and lagged for 20 cm. with asbestos to produce a zone of gradual temperature drop. About 2 hours are required for 0.2–0.5 g. of Os to react. The chloride precipitates in various forms (crusts to powders) and in various colors (black to red-brown). It deposits in the reactor tube at and beyond the construction. The tube is melt-sealed at the constriction, and the part of the tube containing the chloride is evacuated, a cooling trap being inserted before the pump. The material is sublimed in vacuum, using the same tube, and deposited in a further section of the tube.

PROPERTIES:

Black crust with a metallic luster, or red-brown powder. Insoluble in water and other solvents and in concentrated oxidizing acids. Slowly hydrolyzed by water. The above product does not correspond exactly to the composition given by the formula.

REFERENCE:

O. Ruff and F. Bornemann. Z. anorg. Chem. 65, 446 (1910).

Sodium Hexachloroosmate (IV)

$Na_2OsCl_6 \cdot 2H_2O$

In the method of Gutbier and Maisch, fine osmium powder and NaCl are mixed in a 1:1 ratio and the mixture heated in a porcelain boat in a stream of Cl_2 for half an hour, at which point the temperature should correspond to a dull red heat. The conversion to Na_2OsCl_6 is almost complete. The sintered contents of the boat are dissolved in the minimum quantity of cold dilute hydrochloric acid. The unreacted metal is filtered off and the filtrate is saturated with HCl (careful cooling). Most of the excess NaCl is thus separated although part of the Na_2OsCl_6 also precipitates out.

Gradually evaporation of the filtrate yields Na_2OsCl_6 as beautiful crystals, which, however, obstinately retain traces of NaCl even after repeated crystallization from dilute hydrochloric acid.

REFERENCE:

A. Gutbier and K. Maisch. Ber. dtsch. chem. Ges. 42, 4239 (1909).

Ammonium Hexachloroosmate (IV)

$(NH_4)_2OsCl_6$

In the method of Gutbier and Maisch, this salt is precipitated by allowing a dilute alcoholic solution of NH_4Cl to react with the stoichiometric quantity of Na_2OsCl_6 (also in alcoholic solution). The precipitate is a fine, dark-red powder. It crystallizes from dilute hydrochloric acid (or from a mother liquor consisting of the components) in beautiful, shiny black octahedra which are opaque under the microscope.

Gutbier claims that $(NH_4)_2OsCl_6$ is also obtained by dissolving in HCl the sublimates from osmium fusion, concentrating the solution, and mixing the filtered liquid with NH_4Cl.

REFERENCE:

A. Gutbier and K. Maisch. Ber. dtsch. chem. Ges. 42, 4239 (1909).

Osmium (IV) Oxide

OsO_2

Osmium (VIII) oxide is reduced in the cold by a stream of H_2. If, however, the OsO_4 is heated in the H_2 stream, the product is the metal. Osmium (IV) oxide can also be prepared by heating a fine powder consisting of a mixture of K_2OsCl_6 and three times its amount of Na_2CO_3. The temperature should be lower than red heat; the cooled product is extracted with water which is slightly acidified with dilute hydrochloric acid. The product is perfectly pure OsO_2.

Alternate method: Heating of Os to 600-610°C in a nitrogen stream saturated with OsO_4 vapor. Unreacted OsO_4 is reclaimed from the nitrogen stream by cooling it to a low temperature [O. Ruff and H. Rathsburg, Ber. dtsch. chem. Ges. 50, 495 (1917)].

PROPERTIES:

Formula weight 222.2. d 11.4. Black powder. Insoluble in water and acids. Forms OsO_4 on heating in air; readily reduced to the metal by H_2. Crystal structure: rutile type.

Osmium (VIII) Oxide

OsO_4

$$\underset{190.2}{Os} + \underset{64.0}{2O_2} = \underset{254.2}{OsO_4}$$

Pure OsO_4 is best prepared by a dry method. Osmium powder is heated in a boat placed in a glass or quartz tube through which a

stream of dry oxygen is passed. The metal burns to OsO_4, which deposits beyond the heated zone of the tube or, better, in a bulb fused to the tube and cooled in ice. The deposit consists of white shiny crystals, though at first it may be a liquid (occasionally pale yellow in color), which forms a crystalline solid on cooling. Two or three receivers, preferably connected via ground-glass joints, are fitted to the glass tube beyond the bulb. They are half-filled with KOH to absorb the OsO_4 vapor entrained by the oxygen. The OsO_4 in the receivers is reclaimed by reduction to potassium osmate (violet-blue octahedra); this is accomplished by treating the combined caustic liquors from the receivers with an equal quantity of alcohol.

The temperature at the boat is increased gradually so that the reaction does not proceed too vigorously, heating initially to 300°C and gradually increasing the temperature to 800°C. The temperature is then slowly reduced, and the product allowed to cool in the tube. The heating is most conveniently carried out in a small tubular electric furnace.

PROPERTIES:

M.p. 40.6–40.7°C, b.p. 130°C; d 4.9. Soluble in water without decomposition; may be volatilized in steam. Dissolves slowly. Decomposed by conc. HCl with evolution of Cl_2. A solution of OsO_4 is not decomposed by light and can be indefinitely stored in transparent bottles. Toxic; the vapor first irritates the respiratory passages and (particularly) the eyes. Decomposed in a stream of H_2 at red heat, forming a mirror.

Potassium Osmate (VI)

$$K_2OsO_4 \cdot 2\,H_2O$$

A solution of OsO_4 in potassium hydroxide solution is reduced with alcohol.

Osmium powder (2 g.) is heated with 5 g. of KOH and 3 g. of KNO_3 in a silver dish to form a smoothly flowing melt. After cooling, the brown solid is dissolved in 50 ml. of water. The gray-violet crude salt is precipitated by adding twice the volume of alcohol. It is readily decomposed and cannot be recrystallized from water. It is decomposed by heating with 5 g. of CrO_3 and conc. H_2SO_4, the OsO_4 distilling off is collected in 10% KOH, and $K_2OsO_4 \cdot 2\,H_2O$ is precipitated from the resulting solution by adding an equal volume of alcohol. The solid is filtered off with suction, washed with 50% alcohol and with absolute alcohol, and dried in vacuum over H_2SO_4.

In a simpler method, osmium powder is heated directly in a stream of O_2 (compare preparation of OsO_4), and the OsO_4 vapor is collected in 10% KOH.

PROPERTIES:

Pale violet-red octahedra. Readily soluble in water, insoluble in alcohol and ether. Stable only in dry air. The water of crystallization is removed by heating to 200°C in an inert gas. Heating in air produces OsO_4.

REFERENCE:

O. Ruff and F. Bornemann. Z. anorg. Chem. 65, 434 (1910).

Potassium Osmiamate

$K(OsO_3N)$

$$\underset{254.2}{OsO_4} + \underset{56.1}{KOH} + \underset{17.0}{NH_3} = \underset{291.3}{K(OsO_3N)} + \underset{36.0}{2\,H_2O}$$

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In the method of Joly, 100 g. of OsO_4 is dissolved in a solution of 100 g. of KOH in 50 ml. of H_2O; the solution is heated to 40°C and dilute ammonia is added; this clears the dark-brown liquid and precipitates $K(OsO_3N)$ as a granular, yellow crystalline powder.

Excess ammonia should be avoided because it may produce $NH_4(OsO_3N)$. The product is washed with some cold water and recrystallized. Larger crystals may be obtained by gradual evaporation of the solution; however, these crystals are dark due to incipient decomposition.

PROPERTIES:

Fine, granular, yellow crystals. Readily soluble in water, only slightly soluble in alcohol. Darkens on heating to 180°C, with decrepitation at higher temperatures. d 4.5. Tetragonal crystals.

REFERENCE:

A. Joly. Comptes Rendus Hebd. Séances Acad. Sci. 112, 1442 (1891).

Part III
Special Compounds

SECTION 1

Adsorbents and Catalysts

R. WAGNER

Introduction

Solid adsorbents or catalysts must possess large surface areas to allow contact with large quantities of reactants. Large surface areas can be obtained via two methods:

1) SUBDIVISION OF THE SOLID

The solid is subdivided into very small granules so that a large fraction of the total crystal lattice structure becomes exposed as particle surface. Comparison of x-ray and ultramicroscopic data then shows whether the resulting granules are primary particles (i.e., coherently diffracting single crystals) or secondary particles (i.e., a mosaic consisting of several primary crystals).

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2) CREATION OF A NETWORK OF INTERNAL PORES

In this case, the solid is permeated by a system of pores (interconnected or not), somewhat in the manner of a sponge. The net result is the creation of a large internal surface. The pore openings of such active solids should not be too narrow since they must allow the gases to penetrate into the interior (see [8]).

The two methods of achieving high surface may be illustrated on the classic catalyst, platinum; thus, platinum black is the subdivided solid, while platinum sponge is the porous form.

Active substances not only must have a large surface area, but must also possess a proper surface structure. As a general rule, one can expect the surface lattice of metals and ionic compounds to differ from the interior lattice of the crystal [12, 13, 14]. Thus, the active surface is very readily affected by external agents (such as impurities), and is also subject to other influences, such as the method of preparation, etc. In addition, it is often found that the same particle may carry several crystallographically differing surfaces. Obviously, these will differ not

only in their chemical properties [2, 4, 5] but also in their catalytic activity [7, 9, 11]. This fact, as well as the presence of intrinsic and impurity defects in the lattice, results in an overall surface which is usually very heterogenous; this, in turn, affects its adsorptive and catalytic behavior.

The methods of controlling particle size, surface area and surface structure during preparation of various adsorbents and catalysts are given in the preparative directions for individual substances, as well as in the general notes. A more extensive treatment of these problems is given in Ref. [A], especially in the articles in Vol. 4. The usual methods are frequently employed to obtain substances whose activity is not only related to their particle size and surface structure, but is also a direct consequence of other factors such as lattice defects, amorphism, the existence of unstable modifications [1, 10], etc.

We have seen in the above that the activated state of solids, which is the result of the existence of special conditions in the material, is rather unstable and can easily be destroyed. In the preparation of activated solids, this state is fixed by removing the conditions favorable to a transition to a more stable form (for example, slow aging at preparative conditions); i.e., the solid is "frozen" in the activated state. This may be done, for example, by rapid quenching, quick removal of supernatant mother liquors, etc. The active state also implies higher than normal surface energies. For this reason, active materials are generally very reactive, and are frequently used in heterogeneous reactions (solid-solid, solid-liquid, or solid-gas). They are more readily decomposed chemically than inactive preparations; thus, active metals oxidize faster, oxides hydrate more easily, hydroxides and hydrated oxides are more sensitive to CO_2. All of these solids decrease in activity with time, due to a slow healing of surface defects and an eventual increase in grain size. The kinetics of such aging processes are in some ways analogous to those of the ion-hole processes in semiconductors. Aging proceeds via a series of individual steps and, depending on the activation energy of these steps, different optimum temperatures are required if the aging is to proceed at a significant rate. The temperature scale of Hüttig [6], derived as an extension of the work of Tammann (see table), is based on studies of metals and ionic compounds and provides a useful rule-of-thumb guide to the temperatures at which these processes take place.

It is seen from the table that some healing of surface defects is possible without undue reduction of particle size. In general, however, the temperature of any heat treatment of active materials must be strictly controlled to avoid deleterious effects. In heterogeneous gas catalysis, reaction temperatures exceeding those recommended in the table are often unavoidable; this leads to a

Period	α^*	Processes occurring in the catalytic material
Initial surface degradation	< 0.23	Reduction in adsorbing surface; degradation of those surface defects which possess the highest energy.
Surface activation	0.23–0.36	Degradation of surface defects.
Deactivation of the surface	0.33–0.45	Formation of a surface which is stable in a thermal equilibrium; beginning of particle sintering.
Activation of the crystal center	0.37–0.53	Degradation of defects in the interior of the crystal.
Deactivation of the interior of the crystal	0.48–0.8	Accretive crystallization.
Relaxation and disintegration of the crystal	> 0.8	Stage prior to melting.

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*$\alpha = T/T_m$, where T is the temperature of the experiment and T_m the melting point of the substance (°K).

rapid inactivation of the catalyst. In such cases a stabilization of the surface and of the remainder of the defect structure may be achieved by precipitating the catalyst onto a suitable carrier substance. This method is also used to transform into a quasi-solid form substances that, when pure, normally exist only in a subdivided form.

Such carriers must have good accessibility to gases, combined with reasonable mechanical strength and thermal stability. The frequently used carriers are:

NATURAL MATERIALS

Pumice, kieselgur, various silicates (asbestos, meerschaum, etc.), adsorbent clays, etc.

SYNTHETIC MATERIALS

Magnesium oxide, γ-aluminum oxide, synthetic rutile, thorium dioxide, silica gels, barium sulfate, activated carbons, metallic network supporting structures, various silicates (especially of Mg, Al), etc.

Natural materials are transformed into carriers in a variety of ways such as slurrying, washing and treatment with acids or alkalies; or they may have to be fractionated to separate the most active structures before the catalyst itself is deposited. Catalytic substances containing alumina, silica, thoria and similar carriers may also be obtained by coprecipitation.

It is frequently observed that the activity of a catalyst varies with the carrier and substrate and that certain catalyst-substrate combinations give especially good results (see [3]). This is a particular case of catalyst promotion which is frequently observed in mixed catalysts. This phenomenon is of great practical importance. It permits the creation of catalyst mixtures that are very active and capable of influencing reactions in a very specific manner, something that the individual components of the combination cannot achieve qualitatively or quantitatively.

REFERENCES:

[A] Handbuch der Katalyse [Handbook of Catalysis], G. M. Schwab, editor, Vienna, 1940–1957, especially the following:
Vol. 4. Heterogeneous Catalysis I, Vienna, 1943.
Vol. 5. Heterogeneous Catalysis II, Vienna, 1957.
Vol. 6. Heterogeneous Catalysis III, Vienna, 1943.

[B] Advances in Catalysis, Edited by W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, New York, beginning with 1948.

[C] Reviews of patents dealing with the preparation of adsorbents and catalysts appear from time to time in Kolloid-Zeitschrift.

1. R. Fricke. See [A], Vol. 4, pp. 1–150, especially p. 21 ff.
2. R. Fricke. Naturwiss. 31, 469 (1943).
3. A. Guyer et al. Helv. Chim. Acta 38, 960 (1955).
4. K. W. Hausser and P. Scholz. Wiss. Veröff. Siemens-Konzern 5, No. 3, p. 144 (1927).
5. J. A. Hedvall and R. Hedin. Chemie 56, 45 (1943).
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ACTIVE METALS

The usual methods for the preparation of active metals fall into three groups, which are characterized by common preparative methodology and the same type of defect structure of the products.

PREPARATION BY REACTIONS OF SOLIDS

These reactions should be carried out topochemically; i.e., the active metal should be formed in the boundary region of the solid starting substances and not via a reaction between dissolved or gaseous particles. It is also desirable to avoid transport of the atoms of the solid from the initial reaction site; thus, any regrouping of atoms due to the reaction should involve minimum displacement. The desired product should be a loose network of mutually joined primary crystallites. The lower the temperature, the shorter the exposure of the material to high temperature; and the looser the structure of the starting material, the closer the approach to this ideal condition.

Reactions of this type include:

1) Reduction of solids with gaseous agents (see preparation of pyrophoric cobalt, p. 1615; Ni-Mg mixed oxalate catalyst, p. 1615).

2) Reduction of solids with solid reducing agents, solid-solid reactions (see tungsten, p. 1622).

3) Reduction of solids with solutions of reducing agents (see "molecular" silver, p. 1623).

4) Leaching out one component from a solid mixture (see Raney Ni, p. 1625).

5) Thermal decomposition of solids, resulting in liberation of a metal (see nickel formate-paraffin catalyst, p. 1631).

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PREPARATION OF ACTIVE METALS BY DEPOSITION FROM A HOMOGENEOUS MEDIUM

These reactions give materials with a broad particle size distribution, which does not follow a predetermined probability function, but is controlled by the processes of nucleation and phase formation. A precondition for such a distribution is a high degree of supersaturation of the homogeneous phase, something which is readily achieved given the poor solubility and high boiling of metals. One thus obtains many nuclei. Local supersaturation is insufficient and is to be avoided. Processes of this kind involve:

1) Reductions of compounds from the gaseous phase and from homogeneous solutions (see active copper, p. 1633).

2) Thermal decomposition of volatile metal compounds, especially carbonyls (see carbonyl iron, p. 1636).

PREPARATION BY PRECIPITATION ON INTERFACES

The structure of such precipitates can be influenced by the carrier. Thus, oriented deposits are known in which the crystallites of the deposit are preferentially attached to a specific crystal plane of the carrier. Further, there exists the phenomenon of epitaxy, in which the crystal axes of the individual deposit particles have a definite spatial and geometric relationship to each other and to the crystal axes of the carrier. Under such conditions, there may occur significant changes in the relative proportions of some crystal surfaces to the total surface area. Precipitation on a surface is not necessarily preceded by a chemical reaction.

Among such methods of preparations are:

1) Electrolytic preparation of finely divided and active metals (see explosive antimony, p. 1638).

2) Electrochemical reduction, cementation (see silver, p. 1641).

3) Deposition from a vapor (see metallic deposits from a vapor, p. 1643).

Pure metallic preparations normally do not have a very high intrinsic activity; the total activity of a catalyst depends very much on the development of the surface. Lattice imperfections are usually observed only in the presence of impurities (incomplete reaction of starting materials) or in metals supported on carriers. The carriers prevent sintering of metal particles [73] on heat treatment during preparation or use, and in addition they stabilize crystal modifications beyond their normal range of existence.

The extremely active metals are pyrophoric; that is, they oxidize spontaneously on contact with air or in a high-temperature environment, becoming brightly incandescent (spontaneous and latent pyrophoric tendencies, respectively). The spontaneous pyrophoric tendency, which causes some obvious difficulties in the handling of these materials, may be converted to the latent one by mixing the products with a 0.5% solution of acetyl cellulose in acetone or a very dilute solution of polystyrene in benzene, followed by evaporation of the solvent. Frequently, a spontaneously pyrophoric metal may be sufficiently deactivated either by shaking it for some time with pure benzene, petroleum ether, ethanol or a similar substance, or by allowing such a liquid to evaporate from the mixture. On such treatment the particle surfaces become covered with a thin layer of oxide due to slow diffusion of oxygen through the liquid or due to slow exposure on evaporation. Because the exposure is slow and the particle is at least partly submerged in a heat-removing liquid, the heat generated by the oxidation does not increase the temperature to the point of ignition.

Pyrophoric Cobalt

I. $$\underset{183.9}{2\,CoO(OH)} + \underset{67.2\,l.}{3\,H_2} = \underset{117.9}{2\,Co} + 4\,H_2O$$

Cobalt (III) hydroxide (prepared as on p. 1520) is placed in a porcelain boat and reduced in a stream of hydrogen. The boat is heated by a tubular electric furnace whose temperature is regulated by a thermocouple connected to an on-off relay. For practical purposes, a temperature exceeding 300°C gives a sufficiently high reduction rate. The crystal structure and pyrophoric nature of the product (at room temperature) are related to the reduction temperature as follows:

Temperature, °C	300	400	500	600	700	800
Crystal structure	α-Co (hexagonal [49]) . . . , β-Co (cubic)					
Pyrophoric tendency (see p. 1614)	spontaneous		latent	not pyrophoric		

II. CARRIER-SUPPORTED PYROPHORIC COBALT, BY REDUCTION OF A COPRECIPITATE

A solution of 75.0 g. of $Al(NO_3)_3 \cdot 9\,H_2O$ (0.2 moles) in 300 ml. of water is prepared and 200 ml. of 20% sodium hydroxide solution is added with efficient stirring. The initial precipitate is redissolved and a solution of 29.1 g. of $Co(NO_3)_2 \cdot 6\,H_2O$ (0.1 moles) and 20 ml. of conc. HNO_3 (d 1.40) in 500 ml. of water is immediately poured in (thin stream, good agitation). The violet-rose precipitate is allowed to settle and then is washed 4 or 5 times by decanting with pure water. It is then centrifuged off and dried in an oven at 75°C. The coprecipitate is then ground under water and boiled several times with water (250 ml. each time) until the absence of nitrate in the product can be established by some qualitative test reaction. The product is again collected by centrifugation and dried at 75°C, then at 100°C. Reduction of such coprecipates by method I yields spontaneously pyrophoric materials even at the highest reaction temperatures. While β-Co prepared by method I is converted more or less completely to the α-form on grinding in the absence of air in an agate mortar, materials prepared via method II remain completely unchanged [17] on such grinding. The β-form appears to be the more active hydrogenation catalyst [56].

Ni-Mg Mixed Oxalate Catalyst (1:1)

$$(Ni, Mg)C_2O_4 \cdot 2\,H_2O \xrightarrow{(H_2)} Ni/MgC_2O_4$$

In the Langenbeck method [34] a solution of 15 g. of $Ni(NO_3)_2 \cdot 6\,H_2O$ and 70 g. of $Mg(NO_3)_2 \cdot 6\,H_2O$ in 600 ml. of water is heated

to 50°C and the mixed oxalate precipitated by addition of a solution of 29.6 g. of $H_2C_2O_4 \cdot 2\,H_2O$ in 400 ml. of water (constant stirring). The mixture is then left standing for 12 hours to complete the crystallization. The compound is collected by suction filtration and the light-green crystals washed with water until free of nitrates. Drying at 100°C yields 16 g. of the mixed oxalate.

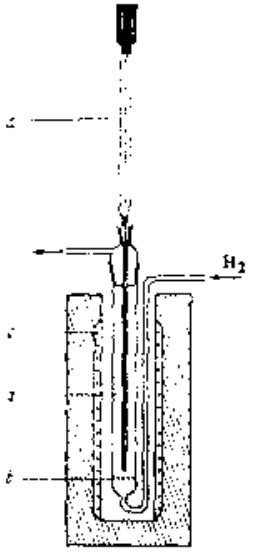

Fig. 336. Preparation of mixed salt catalysts by fluidized bed decomposition of oxygen-containing compounds. *a* reactor, *b* fritted-glass plate (distributor), *c* electric heating coil, *d* thermometer connected to an on-off relay in the heater circuit.

The material is reductively decomposed in the apparatus of Fig. 336. The sample is placed over the fritted-glass plate *b* (which acts as a distributor). When the hydrogen stream is adjusted to 10 liters/hour at STP, the mixed oxalate should form a stable fluidized bed. The temperature is then raised to 350°C. The decomposition takes 150 minutes.

PROPERTIES:

Black, pyrophoric powder. Aside from the metallic Ni produced in the decomposition, contains a nearly unchanged magnesium oxalate carrier [32]. Extremely active hydrogenation catalyst.

GENERAL:

The reduction of oxygenated compounds to active metals presented above is a very general method. Hydrogen is frequently the only useful gaseous reducing agent. It possesses a high thermal conductivity, and therefore the heat of reaction tends to be removed as fast as it is generated. This is important in systems where the metal, once produced, catalyzes another further reaction [2, 52]. Apart from this, fewer undesirable side reactions can be expected with hydrogen than with other (possibly) useful gases such as CO, the lower hydrocarbons and NH_3, with which formation of carbonyls and contamination with carbides and nitrides is possible [20]. The flow rate must be sufficiently high to remove the volatile decomposition products as fast as they are formed; otherwise the reaction may be inhibited and the activity of the final product may be less than the optimum [56, 69, 71]. If necessary, the exit gas composition

may be monitored [2]; a continuous monitoring system based on the thermal conductivity of the gas can be especially useful [8].

The oxygenated starting material must also be carefully chosen. In the following, we shall present some remarks pertaining to individual classes of starting materials.

OXIDES

The best starting materials are active oxides, possibly produced *in situ*, preferably from hydroxides, hydrated oxides or carbonates. In some cases it may be necessary to start with a very well-defined oxide modification in order to obtain an active catalyst [29]. Occasionally, the required starting oxides are produced by thermal decomposition of nitrates. However, the activity of such products is not very high and their maximum specific surface does not exceed a few $m.^2/g$. For this reason, nitrate decomposition is important only for the production of supported catalysts (see below). Oxides calcined at a high temperature, as well as spinel-type materials, should be avoided, since their reduction times tend to be extremely long [2].

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Heavy-metal salts in this class may reduced directly since their anions also are reducing agents and thus promote the overall reaction [36]. In some cases (see p. 1665), simple thermal decomposition of the formate or oxalate will yield the metal; in such cases the hydrogen acts only as a protective gas which prevents reoxidation. Metals obtained by this method are not always completely free from carbon [33, 37]. The nature of the starting material may influence the activity of the product metal catalyst to some extent; this is especially true if the material is reduced at a temperature just sufficient to effect the reaction [42].

The following methods apply to the production of carrier-supported catalysts:

a) Precipitation of the compound to be reduced (hydroxide and carbonate by precipitation from solution, oxide by nitrate decomposition) on the desired carrier. The major methods involved are those of Sabatier [60, 61] and that illustrated by the case of active copper [47] (see copper tower, p. 459). Many industrial catalysts are prepared in this manner; it is especially recommended for cases where the active material must participate in a stoichiometric reaction.

b) Coprecipitation. In this case, the noble and the base metal are both attached to the same type of anion. The noble metal is in the form of a compound which yields the actual catalyst upon reduction, while the base-metal compound yields the carrier upon

reductive decomposition. The coprecipitation must be carried out in such a way as to avoid possible fractionation of the two components [66]. Thus, it is desirable that the coprecipitants form compounds or solid solutions under the mother liquor. It is known for instance, that divalent metal couples (Co/Zn; Ni/Zn [12]) as well as mixed bi- and trivalent metal couples (Mn/Al; Co/Al [13]; Ni/Al [13, 43, 44, 46]; Cu/Al [5]) can form double hydroxides. Solid solutions (or mixed crystals) tend to give especially finely divided active metal catalysts, because this subdivision tends to exist in the material even prior to the reduction. Systematic studies by Langenbeck have shown that mixed formate and oxalate crystals tend to give especially active catalysts. Such mixed salts decompose at low temperatures and the active metal exists in a finely divided form [56]. The specific surface in such cases is high (in isolated cases it may exceed 200 m.²/g. [54, 56]).

To achieve homogeneity with these relatively soluble compounds, which, however, have different solubilities, the mixed formates must be prepared by a special spray-drying technique [31]. The mixed oxalates, which are precipitated with oxalic acid and ammonium oxalate rather than with alkali oxalates (this tends to give more active catalysts), yield, as a rule, homogeneous materials via a simple precipitation. Complex oxalates are just as usable as the mixed oxalates [33].

c) Activation of the surface of suitably shaped metals by surface oxidation and reduction. This process may have to be repeated; highest activation is usually obtained after 3–4 cycles [21]. The product particle consists of a small solid metal nucleus—the carrier—to which the reduced metal, in finely divided or porous form, adheres tightly. The roughening of the surface accompanying this process leads to a useful increase in specific surface. The starting materials are usually thin metal foils, but sometimes oxidized wire cuttings (see CuO "wire" [45]) give a useful catalyst with a carrier of exceptionally high thermal conductivity. This is a useful feature because it helps achieve a uniform temperature distribution within a closely packed catalyst mass.

The above methods may also be used for the production of alloy powders and solid metallic solutions. However, the mechanical properties [24], the tendency to lattice imperfections [25], and the catalytic activity [4, 68] of such preparations are not simple functions of the composition.

The hydrogen reduction method is also used for the preparation of active forms of lower oxides and sulfides of multivalent metals. However, these materials require a much longer time to achieve reduction, even though the procedure is otherwise identical.

The optimum reduction temperature depends on a variety of factors. Among these the nature of the metal is, of course, of primary importance. However, the type of the anion, the purity of

the starting material [51], the degree of decomposition and the defect state of the compound to be reduced are also important determinants of the optimum temperature. The deposition on a carrier or the presence of admixtures [11, 55, 62] may decisively influence the reductive behavior. The lowest reduction temperatures are achieved with specially purified gases (carefully dried H_2 [56], CO free from CO_2), if necessary, at reduced pressure [48].

Literature references dealing with the preparation of active metals by reduction with gaseous agents:

Metal or alloy		Starting material for the reduction					
		Oxide	Nitrate	Hydroxide	Carbonate	Formate	Oxalate
Fe	I	[28]	—	[18]	—	[3]	[3,6,37]
	II	—	—	*a*, *b* [29]	—	—	—
Fe—Cr Fe—Mn	I	[38]	—	—	—	—	—
Fe—Co	I	—	—	—	[68]	[3,38,40]	—
Fe—Ni	I	—	[53]	—	—	[38]	[25]
	II	—	—	—	*a* [10]	—	—
Fe—Cu	I	—	—	[57]	—	—	[24]
Fe—Ag Fe—Au Fe—Pb	I	—	—	[57]	—	—	—
Co	I	—	[53,59]	[17]	—	[39,41,42,56]	[39,42]
	II	—	*a* [59]	*b* [17]	*a* [27]	*b* [56]	*b* [34]
Co—Ni	I	—	[53]	—	—	[38,40]	—
Ni	I	[41]	[15,42,53]	[19,41,42]	[4,18]	[39,41,42]	[9,39,41]
	II	*c* [70]	*a* [64,65]	*b* [14,50,63]	*a* [7]	*a* [58] *b* [30,31,35,54]	*b* [32,34,35]
Ni—Cu	I	—	[53]	—	[4]	—	—
Cu	I	[16]	—	—	[16]	—	[72]
	II	*c* [1,21]	*a* [26,67]	*a* [16,47]	—	*b* [33]	*b* [33]
W	I	[22,23]	—	—	—	—	—

I: free metal or free alloy.
II: metal on supported carriers: *a* deposited by precipitation; *b* deposited by coprecipitation; *c* obtained by activation (see text).

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Tungsten

$$\underset{231.9}{WO_3} + \underset{196.1}{3\,Zn} = \underset{183.9}{W} + \underset{244.1}{3\,ZnO}$$

Small amounts of a homogeneous mixture of 50 g. of finely powdered calcined WO_3 (prepared from analytical grade sodium tungstate) and 150 g. of fine zinc dust (containing as little oxide as possible and dried at 150°C) are pressed into unglazed porcelain crucibles. An unglazed porcelain tube may be used when a larger batch is to be prepared; the tube, centered vertically in the crucible, provides better heat conduction. The mixture is then covered with a 1- to 2-cm. layer of zinc dust, and the crucible is then closed with a closely fitting asbestos lid. To initiate the reaction, the crucible is heated to 500–520°C in an electric furnace. As soon as the mixture ignites and a bright glow is visible through a small hole in the asbestos cover, the current is cut off. The reaction is completed within a few minutes and the crucible may then be removed from the furnace. After complete cooling, the crucible is broken up and the product added (in small portions) to cold, dilute (1:4) hydrochloric acid. The mixture is boiled until hydrogen evolution ceases and the supernatant is of Zn-free acid must be added from time to time). The product is washed in a centrifuge with oxygen-free water; at the end, the wash liquors must be free of chloride ion. Toward the end of the washing procedure, the metal begins to form a colloidal suspension. It should be covered with water at all times to avoid reoxidation. After washing, the water is displaced with ethanol, under which the

product may be stored in active form; or it is inactivated with benzene (see p. 1614) and dried in vacuum over P_2O_5. In the latter case, the product consists of coarse lumps, which may be cautiously triturated under benzene to give a fine powder upon drying [1, 3, 5].

PROPERTIES:

High density black powder which consists of 99% W, provided the workup has been rapid and no oxygen contacted the product. The average size of the primary particles is about 400 A, with the individual crystallites showing a slight lattice distortion [3]. Preparations which are not inactivated prior to storage oxidize in air, evolving heat; after this, they show oxygen bands in the powder pattern.

GENERAL:

This method is obviously applicable only to very high-melting metals which retain their subdivision and defect state in spite of the high reaction temperature. The retention of these properties is aided by the fact that the particles of the reaction product are embedded in ZnO, which, together with the unreacted Zn, gives effective protection against penetration of atmospheric oxygen during cooling. This form of tungsten, as well as the analogously prepared molybdenum [4], consists of such small particles that it gives colloidal solutions on peptization by the etching method (alternate treatment with dilute acids and bases).

Other solid reducing agents include metal hydrides (for example, CaH_2) [2] and carbon. However, reduction with carbon does not yield solid oxidation products and introduces the danger of carbide formation.

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"Molecular" Silver

$$\underset{286.8}{2\,AgCl} + \underset{65.4}{Zn} = \underset{215.8}{2\,Ag} + ZnCl_2$$

In the method of Gomberg and Cohne [3], pure, thoroughly washed silver chloride is placed in a beaker and covered with

water. A platinum disk, attached to a thoroughly flame-cleaned platinum wire, is embedded in the AgCl. A porous clay cell, closed at the bottom and containing some water and a few Zn rods, is placed on top of the AgCl. The reaction starts as soon as the protruding platinum wire is connected to the zinc rods. To increase the reaction rate, a few drops of HCl are added to the clay cell. Reduction of 250 g. of AgCl requires a few days. To decrease the migration of impurities from the zinc into the silver, the liquid level in the clay cell is always kept below that in the beaker. After completion of the reaction, the product (a metal-containing sludge) is washed with water, ammonium hydroxide, again with a large quantity of water, alcohol and finally ether.

PROPERTIES:

High-density gray powder. The individual particles are permeated with many pores (pore radius of the order of 10^4 A); the interconnected single grains are primary particles [8].

GENERAL:

The reduction of a suspended solid is applicable only to noble metals, but under favorable reaction conditions it produces highly dispersed materials [2]. Here again it pays to use very active starting materials, preferably prepared (by precipitation) immediately prior to use. Apart from the galvanic reduction method, one can use dissolved reducing agents. However, these must be absorbed to some extent by the precipitate to be reduced. If the precipitate is unable to absorb the reducing agent, the ions are reduced in solution, with consequent loss of the topochemical nature of the reaction [5].

Reactions of the above type give Cu from hydrated Cu oxide and N_2H_4 [2]; Ag from Ag_2O and H_2O_2 [7]; Ag from AgCl and H_2CO [9], NH_2OH [5], N_2H_4 [6], Cr^{2+} [4]; Pt from PtO_2 and H_2 [1]. Platinum-asbestos and palladium-asbestos may also be prepared by this method (see p. 1563).

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Raney Nickel

I. METHOD OF PAUL AND HILLY [29]

A fireclay crucible is charged with 400 g. of Al. It is then heated to 1200°C, and 300 g. of nickel cubes are added at once to the Al melt. Nickel cubes are especially useful in this case since the material is porous and thus quickly dissolved at the initial, comparatively low temperature. The nickel dissolves in a vigorous reaction which raises the temperature of the melt to 1500°C. The alloy must be prepared under a salt melt layer or in an inert atmosphere to protect the Al from oxidation.

After cooling, the alloy is broken up or cut on a lathe (however, it is best to grind it in a ball mill). Then, 250 g. of the powder is added in small portions to one liter of ice-cold, 25% aqueous NaOH. During the initial vigorous reaction the flask is kept in ice; then, the mixture is gradually heated to 90–100°C and this temperature is maintained until hydrogen evolution ceases. The solid is allowed to settle, the spent hydroxide solution is removed, and the process is repeated twice, each time with one liter of fresh base. The Ni sludge is then washed by decantation with water until the wash water is neutral to phenolphthalein. At the end, the water is displaced with ethanol or dioxane.

II. RANEY NICKEL W-6 [2]

The reactor is a two-liter Erlenmeyer flask equipped with a thermometer and a stainless steel stirrer. This flask is charged with 160 g. of NaOH and 600 ml. of water. The solid is dissolved with intensive stirring and the solution is cooled in an ice bath to 50°C. Then, 150 g. of Raney nickel-aluminum alloy (1 : 1) is added in small pieces. The rate of addition should be such that the temperature of the mixture remains constant at 50 ± 2°C. The addition takes 20–30 minutes. The solution is then stirred for an additional 50 minutes while the temperature is kept at 50°C (first by cooling and later by heating on a water bath). The catalyst sludge product is washed three times by decantation with water. It is immediately placed in the washing tube *c* of the apparatus in Fig. 337 (the last of the product is transferred into *c* with a stream of water from a wash bottle).

Tube c and the one-neck Woulfe flask b are filled with water and the apparatus is assembled as quickly as possible. All rubber stoppers and tubing should be held in place with clamps or wires. Then, O_2-free hydrogen is introduced via e until the entire apparatus is under a gage pressure of 0.5 atm. This pressure is then maintained while stirring at such a rate that the catalyst is fluidized to a height of 18-20 cm. above the bottom of tube c and the wash water flow rate from b is 250 ml./min. When the water reservoir b is nearly empty, stopcocks g and a (the latter is connected to a large pressurized water reservoir) are simultaneously opened, and b is replenished at the same rate as water runs out at g (the flow rate is checked by a differential manometer).

In this way, 15 liters of H_2O are allowed to pass through c. The stirrer motion and wash water flow are then stopped, the pressure is released, and the apparatus is disassembled. The water layer above the catalyst is decanted and the solid transferred into a 250-ml. centrifuge tube by flushing with 95% ethanol. The material is washed three times by stirring (not shaking) with 95% ethanol (150 ml. each time) and the same number of times with absolute ethanol. If centrifuged after each washing at 1500-2000 r.p.m., one to two minutes are usually sufficient to settle out the product. The product catalyst is stored under absolute ethanol in a refrigerator. It cannot be stored indefinitely.

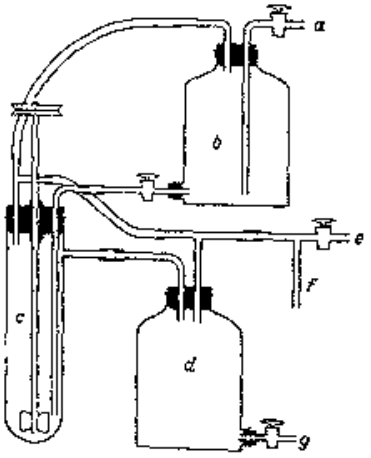

Fig. 337. Apparatus for continuous washing of Raney nickel in the absence of air. a water inlet; b water reservoir; c wash vessel; d discarded wash water; e hydrogen inlet; f nozzle for attaching a manometer; g waste water outlet.

All the above operations should be carried out as rapidly as possible. The time from the beginning of the run to the final placing of the catalyst into cold storage should not exceed three hours.

PROPERTIES:

Very dense grayish-black powder. Used as a hydrogenation catalyst [34]; it can also serve, just as Raney iron or cobalt, as the starting material for the production of the corresponding carbonyl compounds [19]. Also used as a catalyst carrier [9]; can be efficiently activated by treatment with metals of the platinum group [4].

The individual catalyst particles are very porous. The primary particle size ranges from 10 to 100 A [18, 42]. Raney Ni W-6 contains 12.7% Al [20]; its specific surface was determined as 87 $m.^2/g.$ [44].

GENERAL:

The intermediate stages of Raney's [33] general method for the preparation of catalytically active metal skeletons can be varied over a wide range, making possible products of widely varying activities. Let us discuss these individual stages.

The starting alloy is usually prepared by fusion of the components; this fusion should yield as homogeneous a structure as possible [39]. In another method, a fine powder of the pure catalytic metal is mixed with Al powder; the mixture is pressed into tablets and sintered for some time at moderate (of the order of 700°C) temperatures [46]. The Raney alloys can also be obtained by aluminothermic synthesis [11].

The optimum composition of the starting alloy, which determines the catalytic properties to some extent [36], is controlled by several considerations, namely: a) alloys with too high a content of catalytic metal yield products of low activity [6]; the upper limit of allowable active metal content varies from metal to metal. b) Catalysts obtained from alloys of differing active metal contents have somewhat different selectivities in the same reactions [6, 7]. c) Alloys with a definite composition such as NiAl may be so resistant to the leaching solvent used that no useful catalyst results. The use of ordered solid solutions (e.g., Ni_2Al_3) does not offer any advantages, since the Ni atoms tend to regroup into an undesirable configuration after the Al is leached out [42].

Decomposition of the alloy should expose the skeletal metal structure. However, complete removal of the alloying metal (which accompanies the active one) requires drastic conditions and leads to products of poor activity [3]. For this reason the decomposition conditions are selected so as to leave some Al in

the catalyst. The milder the conditions under which the decomposition takes place, the more active the catalyst and the larger the percentage of Al in the final product. In some case, it is sufficient to leach out the surface Al [40, 41; see also 34]. This also permits activation of the walls of the catalyst-containing reactor [38]. It is improbable that the Al in the catalyst is present as Al_2O_3 [20, 45].

Literature references for the preparation of active metals by the Raney process.

Skeletal metal	Second metal (weight %)	Leaching fluid	References
Fe	Al (20/80)	Aqueous NaOH	[17, 30, 34]
	Al	Aqueous NaOH	[15]
Co	Al	Aqueous NaOH	[5, 11, 12, 34]
Ni W-1	Al (50/50)	Aqueous NaOH	[8]
W-2	Al (50/50)	Aqueous NaOH	[27]
W-3, -4	Al (50/50)	Aqueous NaOH	[32]
W-5, -6, -7	Al (50/50)	Aqueous NaOH	[2]
W-8	Al (50/50)	Aqueous NaOH	[25]
	Al	Aqueous NaOH	[6, 29, 39]
	Mg (50/50)	Acetic acid	[28]
Cu	Zn	Aqueous NaOH	[24]
	Al, Zn (50/45/5) (Devarda's alloy)	Aqueous NaOH	[10, 26]
CoNi	Al (2/48/50) (5/45/50)	Aqueous NaOH	[35]
	Si (25/25/50)	Aqueous NaOH	[12]

As far as the effect of the decomposition conditions is concerned, the following can be reported. The activity of the product is proportional to the rate of the decomposition and varies inversely with the decomposition temperature. The rate can be enhanced by starting with as fine metal powder as possible and adding the latter as rapidly as possible to the decomposing medium [6]. The primary particle size of the catalyst (as determined by x-ray analysis) always increases with the hydroxide concentration and the temperature [23]. However, the hydroxide concentration has little effect on the activity of the catalyst. Adkins [1] has presented a number of conclusions on the effect of these external conditions on the preparation of Raney Ni.

MISCELLANEOUS CONSIDERATIONS

In addition to the Al, the ready Raney nickel catalyst also contains hydrogen, to which the pyrophoric nature of the product [22] is due. For the nature of bonding of the hydrogen, see [13, 14, 16, 37, 43]. The removal of hydrogen leads to loss of catalytic activity, which can not be restored by renewed treatment with hydrogen, even though the powder patterns of hydrogen-treated inactive preparations do not differ from those of active ones [22]. Since the catalyst must contain hydrogen, a special technique is required if it is to be used in deuteration reactions [25].

This general method for preparation of catalytically active structures is also applicable to metals other than Ni. It is also useful with alloys [31, 34]. In addition to Al, the alloy component which is leached out may be Si [12], Zn [24] and occasionally Mg [28] (dilute acetic acid is used as the leaching fluid). In determining the optimum composition of the Raney alloy for a specific purpose, one must also take into account the effect of the second metal.

Highly active skeletal Si was obtained by multistage removal of Ca from $CaSi_2$; the silicon metal was arranged in the form of a network consisting of six-membered rings [21].

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Nickel Formate-Paraffin Catalyst

$$\underset{184.8}{Ni(HCOO)_2 \cdot 2\,H_2O} = \underset{58.7}{Ni} + 3\,H_2O + CO_2 + CO$$

Dry, precipitated $NiCO_3$ is dissolved in a 20% stoichiometric excess of 50% formic acid (80°C). The salt that crystallizes on cooling is filtered and dried at 110°C. Then, 100 g. of this formate is placed in a 500-ml. round-bottom flask equipped with a 12-mm. I.D. condenser tube (method of Allison et al. [1]) and slowly heated in aspirator vacuum together with 100 g. of paraffin wax and 20 g. of paraffin oil. The evolving gases are washed three times with paraffin oil to trap entrained paraffin wax which might plug the tubing. The product is then held for one hour at 170–80°C to remove the water of crystallization, and then the temperature is raised to 245-255° to decompose the formate; the termination of the reaction after an additional four hours can be recognized by a decrease in pressure. The reaction product is poured onto a metal sheet while still hot. After cooling as much as possible, the top paraffin layer is scraped off and the remaining very black mass is broken up into coarse pieces. Immediately before use, these paraffin-coated pieces are treated on a large Buchner funnel with a large quantity of hot water to remove most of the paraffin. The residue is dehydrated with pure ethanol; it is then immersed several times in petroleum ether, removing the petroleum ether by suction.

PROPERTIES:

Loose, black, nonpyrophoric powder; relatively stable in air, provided the paraffin is completely removed and well wetted by water. Shows an activity level similar to that of Raney Ni in hydrogenation of aromatic nitro compounds in aqueous solutions.

GENERAL:

Thermal decomposition of some metal compounds whose anions are reducing agents gives the metal, which may have a very high catalytic activity. The active metal may then react with air or with gaseous reaction products. If air is not allowed to penetrate (the reaction is conducted in an inert liquid), and the nascent gaseous products are quickly removed (use of high vacuum or a stream of inert gas—see use of H_2, p. 1616), it is sometimes possible to obtain the metal in its active form.

The following starting metal compounds can be used in this procedure.

Hydrides, for example, CuH [16], ZnH_2 [15], CeH_3 [5], UH_3 [8] and so forth; these are decomposed in high vacuum at relatively low temperatures. Active uranium prepared from UH_3 has the remarkable ability to absorb large quantities of H_2, O_2, N_2, CO, CO_2 and other "base" gases; it can thus be used for the purification of "inert" gases, especially in closed systems [4].

Formates, for example, those of Co [17], Ni [2, 9, 17] and Cu [17]. Decomposition of these compounds yields a very porous active metal structure of crystallites; the same is true of Ni and Co oxalates [3, 13]. The decomposition of these salts is, to a large extent, a topochemical reaction, in which the nascent free-metal atoms regroup themselves within a very small region. To obtain these metals in the form of carrier-supported catalysts, one can start with a mixture of salts [3].

A number of other organometallic compounds among them several acetylides [7] and nitrides, give the metal in a more or less pure form on thermal decomposition.

Finally, active, sometimes even pyrophoric metals can be obtained by thermal decompositions of **amalgams**. Thus, fine powders of Be [14], Cr [6] and Ni [9, 10] are obtained from their amalgams upon removal of Hg by distillation. Since electrochemically obtained Fe and Co amalgams [10, 11, 12] decompose spontaneously, the active metal can be separated by simple mechanical means. This type of cobalt is an extremely active hydrogenation catalyst, while Ni produced from an amalgam is totally inactive [10].

Highly active noble metals may also be generated from other compounds. Thus, Pd, Ir and Pt "sponges" are obtained upon calcination of their ammoniumhexachloro complex salts (see p. 1562).

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Active Copper

$$\underset{63.5}{Cu^{2+}} + 2\,\underset{104.0}{Cr^{2+}} = Cu + 2\,Cr^{3+}$$

A fresh solution (800 ml.) of anhydrous Zn-free $CrCl_2$ (80 g.) is prepared in water strongly acidified with HCl (see p. 1367). Carbon dioxide is bubbled through and the solution is cooled to 0°C. Then, an ice-cold solution of 60 g. of $CuSO_4 \cdot 5\,H_2O$ in 350 ml. of water is added with vigorous stirring. The reduction starts immediately and ends in a short while. The precipitated copper powder is washed several times by decanting with water. The water is then displaced with ethanol. The alcohol is, in turn, displaced with ether or benzene. The product may be stored under either of these liquids, unless it must be inactivated before use (see p. 1614).

DropBooks

PROPERTIES:

Extremely fine red powder with no metallic luster. Very useful as a catalyst in organic chemistry [16, 17].

GENERAL:

The usefulness of this homogeneous phase reduction is restricted to the more noble metals. The range of reducing agents which can be used here is quite wide: cations of low valence (Cr^{2+}, Fe^{2+}, Ti^{3+} and others), reducing anions ($S_2O_4^{2-}$, $PH_2O_2^-$, $HCOO^-$), as well as H_2O_2, N_2H_4, NH_2OH, H_2CO and so forth may all be employed.

These reductions require, as a rule, quite specific reaction conditions, especially as far as the hydrogen ion concentration

and temperature are concerned. Both of the latter factors also affect the particle size of the product: the temperature does so in the way one would expect, but the pH in a less predictable fashion. Thus, for instance, gold precipitates from alkaline solutions in smaller primary crystallites than those obtained from acidic solution [8]. Certain reactions require above-atmospheric pressures [6, 10].

Homogeneous phase reductions have also been carried out in liquid NH_3 [1-5, 22-30]. The use of this solvent extends the general method to less noble metals, whose halides may thus be reduced with alkali metals. The intermediate compounds used are frequently metal *ammines*; these are carefully decomposed to give the active metal. The activity of the product increases with the atomic weight of the reducing alkali metal [26]; it is frequently maximum when Ca is the reducing agent [4, 5]. Many metals obtained via this procedure have remarkable catalytic activities. The use of the method is restricted by the tendency of many of the metals to combine with the reducing agent under the reaction conditions. Also, some of these metals undergo irreversible reactions with the solvent [2]. Solid solutions may be precipitated from solutions which contain two easily reduced cations (see below). Since the free energy of the less noble metals decreases as a result of formation of mixed crystals with more noble metals, the aqueous-solution procedure is not restricted to the alloys of noble metals. If the more readily reduced metal is also quite insoluble under the reaction conditions, it yields the nuclei upon which the remainder of the precipitate crystallizes. Such precipitates are, in general, finer and have a much narrower particle size distribution than chemically uniform materials [14, 24].

Precipitation from aqueous solutions:

Metal	Reducing agent	Reaction medium	References
Cu	Cr^{2+}	acid	[7, 16, 17]
	$S_2O_4^{2-}$	ammoniacal	[9]
Ni	$PH_2O_2^-$	neutral; ammoniacal	[6, 10]
Ag	N_2H_4	ammoniacal	[19]
Pt (Pt black)	$HCOO^-$	neutral	see p. 1562
Au	H_2O_2	alkaline	[8]
	NH_2OH	—	[20]
Ag-Au	Fe^{2+}	acid	[14]
	H_2CO	alkaline	[12]
Ag-Hg	H_2CO	alkaline	[11]

Precipitation from solutions in liquid ammonia:

Metal	Reducing agent	References	Metal	Reducing agent	References
Fe	K	[23]	Ru, Rh, Pd	K	[29]
Co	K	[25]	Ag	Na, K, Ca	[1, 3, 4]
Ni	K	[5, 22, 24]	Ir	K	[28]
	Li, Na, K, Rb, Cs	[26]	Pt	K	[27]

Homogeneous reductions may also be carried out in the gaseous phase. In this case, the product metal must form a sufficiently volatile reducible compound (chlorides are frequently useful in this respect) and the reduction temperature must not be too high. Suitable reducing agents are the vapors of easily volatile base metals or hydrogen:

$$SiCl_4 + 2Zn = 2ZnCl_2 + Si \quad [15]$$
$$TiCl_4 + 4Na = 4NaCl + Ti \quad [18]$$
$$VCl_4 + 2H_2 = 4HCl + V \quad [13]$$

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Carbonyl Iron

$$\underset{195.9}{Fe(CO)_5} = \underset{55.9}{Fe} + \underset{140.1}{5\,CO}$$

I. "FIBROUS" IRON

In the method of Beischer [1], a nitrogen stream saturated with $Fe(CO)_5$ at some temperature is combined in the bulb-shaped reactor of the apparatus shown in Fig. 338 with a stream of very hot nitrogen. The hot-gas quantity is always several times that of the cold one. Thus, for example, if the carbonyl-saturated N_2 flows at a rate of 2 liters/hour, the flow rate of the hot N_2 must be 40–100 liters/hour. If the reaction temperature is maintained between 200 and 700°C and the Fe concentration in the decomposition zone does not exceed 10 mg./liter, a uniform, fibrous product collects in the settling chamber.

PROPERTIES:

Fibrous carbonyl iron, prepared at 200°C and at a reactor concentration of 1 mg. of Fe/liter, quickly absorbs 10–15% of its weight in O_2 upon exposure to air; it must therefore be handled

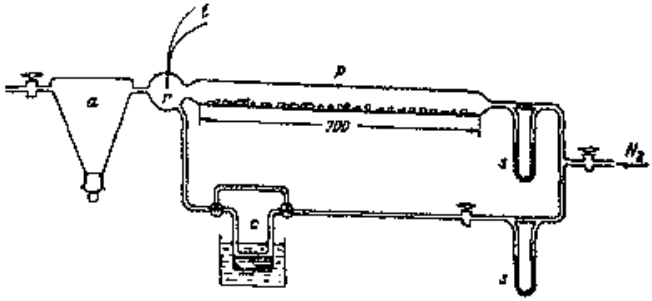

Fig. 338. Preparation of very fine iron powder with fibrous particles. *a* settling chamber; *r* reactor (30 mm. I.D.); *t* thermocouple; *p* nitrogen heating tube (20 mm. diameter), filled with small porcelain pieces, and heated either electrically or with a series burner; *s* flowmeter; *c* carbonyl storage.

and used in an N_2 atmosphere. The individual fibers reach a length of 10^6 A at a rather uniform thickness of about 2000 A. They consist of primary particles 70–90 A long (as determined by x-ray analysis).

DropBooks

II. IRON GLOBULES

In the method of Beischer [1] iron globules are formed at the maximum possible $Fe(CO)_5$ concentration in the decomposition zone. The apparatus of Fig. 339 is used. The air is flushed out with a moderately fast stream of N_2 introduced via the inlet tube to *a*. Then the liquid carbonyl compound is vaporized at a rate of 30 ml./hr. and the vapor fed into the decomposition chamber, which is heated to 200–600°C (depending on the reaction conditions). At this point the N_2 flow is either reduced or shut off completely. The tubing from the distillation flask to the decomposition tube (which is surrounded by a vertical heater) must be well insulated or maintained at about 110°C by means of a small electric coil or tape in order to avoid decomposition of the iron carbonyl. The first crop of product does not have the desired properties. A uniform powder consisting of microscopic globules is obtained only after a certain induction period.

PROPERTIES:

The individual globules have a diameter of 10^4–10^5 A and a peculiar structure similar to onion skin [5]. They contain (probably due to catalytic decomposition of CO on their surface) about

1% C, and they pick up 1-2% O_2 on exposure to air. The particles grow rapidly when heated to above 350°C [4]. Because of its particle size carbonyl iron is useful in solid-solid reactions (e.g. in metallurgical sintering processes).

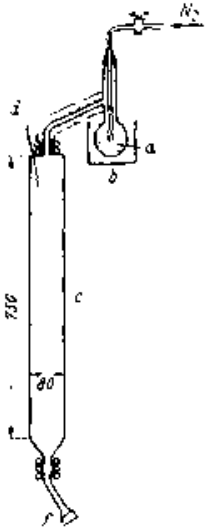

Fig. 339. Preparation of very fine iron powder with globular particles. *a* iron carbonyl distillation flask; *b* oil bath; *c* decomposition reactor and furnace; *d* thermocouple; *f* filter.

GENERAL:

The process may also be used with other metals that form volatile, readily decomposed carbonyls. The optimum reaction conditions vary from case to case. In some instances, suppression of carbide formation is the major problem [2].

A material with a developed inner structure (i.e., porous) is developed if the decomposition is carried out completely in the reactor chamber (whereby the heat is supplied by radiation or hot gases). If the reacting gases are also made to follow a vortex path, then uniform, small particles are obtained [3]. However, any undecomposed carbonyl which reaches the wall of the vessel decomposes on it, precipitating the metal in the form of a tenaciously adhering mirror or in layers of leaflets (see p. 1644). Incomplete removal of air or deliberate addition of oxygen to the reactor may produce fine metal oxide aerosols (see p. 1669).

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Explosive Antimony

A 25% solution of $SbCl_3$ in 10% hydrochloric acid is electrolyzed at 20°C in the apparatus shown in Fig. 340 [6]. The solution is

obtained by adding 300 ml. of conc. HCl to 500 ml. of water, dissolving 250 g. of $SbCl_3$ in this mixture, and adding water to make up one liter. The electrolysis vessel, placed in a constant-temperature bath, is either a 650-ml. three-neck Woulfe flask or a one-liter filter jar [7]. The anode *a* consists of very high-purity antimony; if it is short and does not protrude from the electrolysis jar, it is extended with a platinum wire, the remaining length being supplied with a copper wire. The cathode *c* is best prepared from a 10-cm.-long piece of 1-mm.-diameter Pt wire, but copper [7] or manganin [18] wires of the same diameter are also suitable; the cathode *c* is bent to a U shape and rigidly attached to the stirrer (with the two free ends directed downward). The electrical connection is made via a drop of mercury placed inside the hollow stirrer shaft; this pool contacts a sealed-in platinum wire, which in turn makes contact with the cathode wire.

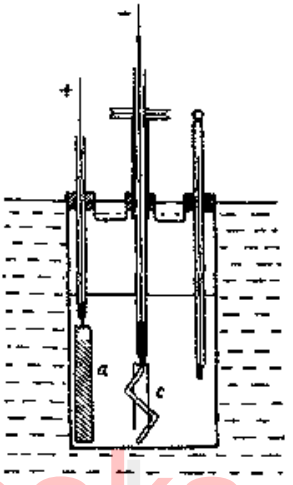

Fig. 340. Preparation of explosive antimony. *a* anode of pure antimony; *c* cathode of platinum wire.

The electrolysis is started at a very low current; after five minutes the current is increased to give a cathode density of approximately 0.3 amp./in.^{2}, while stirring at a rate of 1000 r.p.m. Since the cathode surface gradually increases during the run due to deposition of the smooth, shiny metal, the current must be gradually increased (25% in two hours). A two-hour run yields about 400 mg. of metal deposit, sufficient for demonstration purposes. After completion of the electrolysis the cathode is carefully removed (avoid bumping against the vessel wall), washed with conc. HCl, then with water, and rinsed with alcohol and ether.

PROPERTIES:

X-ray analysis [8, 10, 11] indicates that explosive antimony is amorphous, with a crystal structure almost like that of a liquid except for some short-range ordering of the atoms. This state is stabilized by small amounts of $SbCl_3$ or SbOCl, which contaminate the precipitate. The electrical conductivity is 4–5 orders of magnitude smaller than that of the pure element [4, 18]. Crystallization, which is a first-order reaction [4], may be initiated by scratching the walls, by slight heating, or by an electric discharge. Due to a

"heat of crystallization" of 2.5 kcal./g.-atom [5, 7], the trichloride is vaporized and becomes visible as a fog.

GENERAL:

Good cathodic deposition of metal powder or sponge is controlled by a number of factors which depend on the material itself and on the experimental conditions employed [14, 20, 21].

a) *Cathode surface conditions.* A low concentration of the deposited ion in the cathode surface film tends to prevent the formation of a solid deposit layer, as the crystals then tend to grow away from the surface. Low surface concentrations are enhanced by the use of a dilute electrolyte, complexes in which the metal is firmly bound, the presence of high concentrations of neutral salts, low solution temperatures, and high current density in an unagitated electrolyte.

b) Low overvoltage of the metal to be deposited; this causes needlelike and dendritic deposits which are easily crushed to a crystalline powder, e.g., Cd [19]. The overvoltage of the metals generally increases with complex formation and decreases with increasing temperature. These factors therefore work in a direction exactly opposite to that cited under (a).

c) Coprecipitation of basic salts from the cathode film also gives a porous precipitate, a condition favored by the use of neutral or weakly acid solutions (depending on the tendency of the metal ion to hydrolyze). It is, however, also possible to remove H^+ from the cathode film; this can be done by electrolytic deposition of electron-bearing ions (low cathode current yield)—a factor which may be enhanced by metallic impurities or low hydrogen overvoltage—or by oxidizing agents which use up H^+ while accepting electrons. The effect of temperature on this coprecipitation varies: higher temperatures favor hydrolysis, but also favor the increased supply of hydrogen ions from the solution by increasing the diffusion rate.

An appropriate selection and balance of these factors should permit electrolytic production of powders of every metal that can be deposited from aqueous solution. The particle size of the cathode deposit can be reduced by the use of ultrasound [2, 3].

The simultaneous evolution of H_2, which is not absolutely essential for the preparation of metal powder, nevertheless causes a certain fluffing of the metal precipitates, allowing them to occlude considerable amounts of nonmetallic impurities from the electrolyte. Thus Cu or Ag precipitates may, under proper electrolysis conditions, occlude several percent of citric or tartaric acids (or their salts), as well as asparagine, and so forth. In this state the powders have lower negative potentials than the pure metals [15], in the same way as explosive antimony [18].

Fused salts (fluorides, chlorides) easily yield metal powders [1] because they have virtually no overvoltage as long as the bath temperatures are kept low.

The following metal powders have been obtained by electrolysis of aqueous solutions: Fe [12, 20, 21], Ni [12, 20, 21], Cu [12, 16, 20, 21], Zn [12, 13, 20, 21], Ag [17], Cd [19, 20, 21], Sn, Pb [12], Ni–Pd alloy [9].

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Silver

(Active Agent for Reductors)

$$\underset{339.8}{2\,AgNO_3} + \underset{63.5\,(65.4)}{Cu\,[Zn]} = \underset{215.8}{2\,Ag} + Cu(NO_3)_2\,[Zn(NO_3)_2]$$

A sheet of electrolytic copper [7] or several zinc rods [2] are suspended in a well-stirred solution of 29 g. of $AgNO_3$ in 400 ml.

of water acidified with a few drops of HNO_3. The reaction starts immediately. When the solution is free from Ag^+, the copper sheet and the stirrer are removed and the silver sludge is washed several times with dilute sulfuric acid (decantation). This removes most of the copper (zinc); the sludge is then transferred to the reductor tube and further washed with dilute sulfuric acid until free from Cu (Zn). The sulfuric acid is then displaced with 1N HCl; the acid must always cover the silver in the reductor, whether it is being used or just stored. Any air bubbles present are removed by shaking.

The regeneration of the silver in the reductor proceeds via method of Wislicenus [9]. A small piece of zinc is placed on top of the silver filling of the column (this column packing is blackened for about 3/4 of its length by superficial chloride formation). The reductor should be filled with dilute sulfuric acid. The reduction of the AgCl proceeds rapidly if the Zn makes good contact with the reductor material.

PROPERTIES:

Fine silver-gray powder; used in analytical chemistry as a packing for Jones reductors (reductions in hydrochloric acid solutions).

GENERAL:

This process does not usually yield very pure products [4, 6]. The less noble metals (e.g., Cu [4]) become pyrophoric at low temperatures. The somewhat higher energy level of these preparations is due to the large surface area and to lattice defects. Some metals tend to form fibrous structures [8] with appropriate reducing metals and solvents.

Zinc can also be used as a reducing agent for the preparation of Cu [4, 5], Ni [3] and Sn [1].

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Deposition of Metals from the Vapor Phase

Deposits of metals from the vapor phase [2, 5, 6, 10] are especially useful for studies of very pure materials, where it is desired to correlate the structure and the electronic state of a solid with its catalytic activity. Metal deposits can be investigated by electron diffraction, conductivity measurements, and optical and magnetic techniques even while they are covered with a layer of adsorbed material or while actually participating in a catalytic process.

The experimental apparatus varies with the type of study. In general, the parts of a glass apparatus should be fused together so as to avoid greased glass joints. This means that not only the reaction vessels proper but all the auxiliary devices such as gas receivers, cold traps, manometers and so forth must be fused to the apparatus prior to the start of a run. To obtain reproducible results, the catalyst carrier is carefully purified prior to sealing the apparatus, heated slowly to 400–500°C, and baked at this temperature for several hours in a high vacuum. Only then is the carrier temperature adjusted to the level required for condensation and the deposition of the metal vapor started. All these operations must be carried out in the vacuum of a running pump. Fresh metal deposits adsorb gases extremely readily. For this reason all gases other than those actually needed in the process (especially those which may be catalyst poisons) should be removed from the apparatus prior to the start of deposition.

Reaction vessels: The inside wall is usually used as the support for the deposit. The vessels, which are made of quartz or glass, are of two common types: spherical flasks for adsorption measurements [1, 29] and cylinders, which are especially suited for experiments in catalysis [5, 22]. Since the studies are usually conducted at constant temperature, the wall must have good thermal conductivity. The vessel is either immersed in a bath or surrounded by a jacket filled with a heat transfer medium.

Vaporization of the metal: The metal must be melted in vacuum. Aside from this requirement, which applies in all cases, the experimenter can choose from a variety of options. The usual procedure involves resistance heating of a suitably shaped wire coil. This method can be used where the metal has a sufficiently high volatility below the melting point to produce the vapor at an appreciable rate. In other cases it may be necessary to vaporize the metal at or above its m.p. In these cases, it is

vaporized from the surface of a resistance-heated spiral or boat made of a high-melting metal (W, Mo or Ta). The current leads are sealed to the glass vessel; if necessary, they may be introduced in water-cooled ground joints. Suitable sheet-metal screens prevent condensation of metal in unwanted places.

Additional possible heating methods include high-frequency induction heating and cathode sputtering. However, one should remember that deposits obtained from a vapor and from a sputtered cathode differ somewhat in structure [14].

Condensation. In general, the condensation conditions greatly affect the secondary structure and the catalytic activity of the metallic deposit [7]. Depending on condensation conditions, the metal layers deposited on amorphous supports (glasses) at low temperatures may be either crystallographically disordered (random) or oriented [5, 25]. In an oriented layer the crystallites adhere to the support in a uniform fashion, the boundary with the support being the simply indexed crystal lattice plane that has the lowest atomic (or molecular) density. The crystallite arrangement in all other directions is totally random. Epitaxial growth may occur on crystalline material, with deviations of up to 15% in the lattice dimensions [8, 24, 34]. Metastable crystal modifications have also been observed in vapor deposits [11].

Condensation at low temperatures favors the formation of homogeneous mirrors, which remain stable at room temperature. Under these conditions mirrors are formed even by metals that otherwise would appear dull [28]. The specific surface area, which is controlled primarily by the melting point of the metal, is slightly higher in deposits obtained at low temperatures than in those produced at 0°C [32]. Higher condensation temperatures or the presence of inert gases (noble gases can be used in all cases, nitrogen sometimes, while hydrogen is completely unsuitable; see [12]) results in a decrease of the orientation of the crystallites (the latter cease to be oriented at sufficiently high condensation temperatures). An additional phenomenon appearing at high condensation temperatures or in the presence of gases is that the individual crystallites become smaller while retaining their normal lattice constants [20] and the deposits become dull black. In contrast to mirrors, they show a strong small-angle x-ray scattering [9].

Simultaneous deposition of lattice-distorting substances (NaCl, H_2O) has been recommended for obtaining defect structures [12].

Metal deposits which are useful for preparative purposes may be obtained by **thermal decomposition** of suitable volatile metal compounds (hydrides, carbonyls) on hot surfaces. For instance, decomposition of $Ni(CO)_4$ on Pyrex glass wool at 150°C produces a deposit of very finely divided nickel, which is an excellent catalyst for gas-phase hydrogenation of olefinic double bonds [4].

Literature on metal deposition from a vapor

Metal	Studies on the properties of the deposit	Adsorption measurements	Catalytic studies
Fe	[13, 14, 32]	[3, 21, 33]	[18, 27]
Co	[13]	[21]	
Ni	[5, 7, 11, 13, 20, 25 32]	[5, 7, 26, 29, 33]	[5, 15, 16, 17, 18, 22, 23, 27, 30]
Cu	[9, 13, 19, 28]	[1]	
Rh	[32]		[16, 17, 18]
Pd			[16, 17]
W	[32]	[31, 33]	[17, 18, 27]

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DropBooks

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HYDRATED OXIDE GELS

The hydrated oxides used as adsorbents are called, more precisely, xerogels* or aerogels. They are prepared by drying the corresponding hydrogels. The adsorptive capacity of the xerogels depends on the drying process used. The starting hydrogels are prepared by the following methods:

PRECIPITATION REACTIONS

The molecules of precipitated hydrogels are usually arranged in a random order. However, ordered structures may form if the conditions are such that basic salts or aggregated anions can be produced during the precipitation or when such starting materials are used. The surface properties and pore structure of these gels, which show aggregates of submicroscopic globular particles under the electron microscope, depend on the precipitation reaction used. Among these reactions are:

1) Precipitation with an acid or a base (see hydrated chromium oxide gel, p. 1648; silica gel, p. 1648).

*Translation Editor's Note: In American practice the term "xerogel" is little used, although more precise. We prefer "resin" for organic materials and "dry gel" for inorganic ones.

2) Hydrolyses of alkoxides that give preparations free of electrolytes (see aluminum hydroxide gel p. 1652).

REACTIONS OF SOLIDS

These reactions should be topochemical and may use preformed starting materials. Among the preparative methods of this class are:

1) Topochemical hydroxide formation [see "glimmering" iron (III) hydrated oxide, p. 1654].

2) Leaching out one component of a solid mixture (see p. 1656).

The preparation of gels by controlled coagulation of sols is used more rarely. However, it may still be of interest in special cases. For instance, globular gel particles, which are useful as fluidized bed catalysts, are obtained by allowing the sol to drop into a medium which causes its spontaneous coagulation.

On simple drying in air or heating (if necessary), gels obtained by precipitation reactions show a much higher shrinkage than those obtained by reactions of solids. The shrinkage may, however, be avoided to a large extent if instead of drying the material one displaces the water with organic solvents of low surface tension. These are then removed by evaporation. In general, the pore volume increases as the surface tension of the liquid used decreases [7].

DropBooks

Aerogels with an especially high surface activity and specific surface (up to 800 m^2/g. [4]) are obtained via the procedure of Kistler [5, 6]. In this case, the water in the hydrogel is displaced with an organic liquid which is miscible with water. The preparation is then heated in an autoclave to a point above the critical temperature of the solvent where the supercritical vapor is released. Gels prepared by this method retain the volume and the structure that existed prior to drying. In the preparation of hydrated oxide gels, one must remember that the reaction products age rapidly on contact with the aqueous mother liquor; in addition the aging process is markedly affected by the electrolyte content of the solution. Only a few precipitates remain amorphous for any length of time; most convert fairly rapidly to crystalline hydroxides or hydrated oxides [2, 3]. However, their gel nature initially remains almost the same. Some hydrated oxide gels must not be heated above a certain temperature during drying to avoid spontaneous crystallization with glimmering deflagration (compare also metamictic minerals [1, 8, 9]).

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Hydrated Chromium Oxide Gel

$$\underset{(9\,H_2O)\ 800.4}{2\,Cr(NO_3)_3} + 6\,NH_3 = \underset{152.0}{Cr_2O_3 \cdot (aq)} + 6\,NH_4NO_3$$

Slightly more than one liter of 0.12M NH_3 solution is added with efficient stirring to one liter of 0.04M $Cr(NO_3)_3$ (the excess of NH_3 favors the formation of a flocculent precipitate). The precipitate is washed 10 times by decantation with water, filtered and dried at 150°C [5].

PROPERTIES:

Dark-green glasslike granules. The N_2 absorption isotherm gives a specific surface of 310 m^2/g. (BET method) [5]. Used as a hydrogenation and dehydrogenation catalyst [18].

Silica Gel

To start with, 3.4 liters of sodium silicate solution (sodium waterglass, d^{20} 1.37) is diluted with one liter of water (mechanical stirring). Then, 10N HCl is added at a rate of 10 ml./min. until thymol blue shows an acid reaction (pH 2-2.8). (After addition of 400 ml. of the acid the mixture becomes viscous and rubberlike. The acid addition is interrupted and the mass is broken up. It is then manually stirred while acid is added in drops. The mixing is continued until a thin suspension is obtained. The remainder of the acid is then added at the original rate until the desired pH is reached.) The mixture is then stirred for two additional hours at room temperature, suction-filtered and washed until the wash liquid is no longer acid. The gel is dried at 200°C for 12 hours, ground to the desired particle size, and finally washed free of Cl^-.

The product is then dried at 250°C for 24–48 hours [11]. Yield: 1.5 kg.

PROPERTIES:

Dull-white gel granules; hardness approximately that of glass; high specific surface (500 m^2/g.). Gels prepared according to the above directions are especially useful for chromatographic purposes [11].

GENERAL:

Many other hydroxide precipitates may be obtained in a way similar to that used for the hydrated chromium oxide gel. However, when selecting the starting metal salts one must remember that anions of multivalent acids, especially SO_4^{2-}, are frequently difficult to remove from the product by washing. For this reason nitrates, chlorides and perchlorates are preferred. In addition, hydrated oxides obtained from sulfates frequently have a very high tendency to spontaneous deflagration. Isomeric hydrated salts, such as chromium (III) chloride hydrates, may give a variety of hydroxide precipitates ([10]; see p. 1345). The base is usually a freshly prepared, carbonate-free NH_3 solution. In cases when the metal ion forms stable ammine complexes which make a quantitative precipitation difficult, the precipitation may be carried out with ammonium acetate or tetramethylammonium hydroxide solutions [22]. In addition to these agents and the various alkali metal hydroxides, active MgO and alkaline earth hydroxides may also be used as precipitants. The impurity cations that are adsorbed on the precipitate may, under certain circumstances, act as catalyst or adsorption promoters. Hydrated oxide gels of amphoteric metals may also be obtained by careful neutralization of the corresponding alkali hydroxometallate solutions. As a rule, such precipitates are microcrystalline and contaminated with large amounts of alkali ions. Hydrated oxides of cations with a high ionic potential, such as Ti^{4+}, may also be obtained by hydrolysis of their salts, whereby a dialyzer may also be used [28, 33, 34].

The quantity of the precipitating agent has a large effect on the properties of the product gel. Incomplete precipitations (final acidic solution in the case of hydrated metal oxide gels, final alkaline solution in the case of silica gels) produce soft, friable, strongly opalescent gels with a wide range of pore sizes and low specific surfaces. An excess of the precipitating agent, on the other hand, usually causes the condensation reaction to go to completion. As a result, the gel products are thoroughly cross-linked and the presence of the three-dimensional network makes them hard, elastic and translucent, with fairly uniform pore size.

The properties of the product gels depend also on the reaction temperature, as well as the order and rate of addition of the reagent solutions. If the precipitating agent is added slowly to the salt solution, there is a possibility of forming an intermediate basic salt [12, 24]; these may then precipitate as well defined compounds [6]. On the other hand, slow addition of the precipitant may yield isopolyanions (polysilicate ions and so forth); these last may also be added beforehand to obtain special effects. Such precipitation products are aged in a specific way compared with gels obtained by fast addition of the salt solution to the precipitant [17, 20].

The adsorptive selectivity of the gels may be influenced to a certain extent by the preparative conditions. One may, for instance, produce silica gels which adsorb a specific dye of characteristic molecular shape and charge distribution. This is done by dispersing this dye in the silicate solution and the precipitating the gel in the presence of the dye [2, 4, 9]. Similar experiments have been carried out with optically active compounds ([3], see also [1]). The silica gel surface may also be modified in a specific way by adsorbing on it appropriate substances; this yields preparations with completely new adsorptive properties [14, 19].

The adsorptive activity of gels is reduced not only by heat but also by grinding. Grinding produces a slight reduction in the specific surface. This is occasionally accompanied by a reduction of the average pore radius [16].

The above general remarks apply also to mixed precipitates of metal hydroxides as well as to silica–hydrated metal oxide mixed gels. As would be expected, products obtained by simultaneous precipitation of two (or more) compounds differ from those obtained by mechanical mixing of finished gels; both of these types of gels are in turn different from mixed gels produced by sequential precipitation in the same solution. Finally, we should mention the so-called chalky silica gels (see p. 1656).

To summarize, the quality of the final product gels depends on the history of the preparation. In view of the many possible slight variations in the procedure which affect the reactions involved, it is not surprising that the products vary in quality.

The product gels may be freed from impurity ions (usually present in large amounts) by dialysis or electrodialysis. However, even this procedure does not yield gels completely free from electrolytes. If completely pure products are desired, it is best to use the hydrolysis of alkoxides presented on p. 1652.

Finally, let us cite a number of new publications dealing with the preparation and testing of hydrated oxide gels: hydrated aluminum oxides [30, 32]; silica gels, unmodified [11, 13, 16, 21, 27]; silica gels, modified [1-4, 9, 14, 19]; hydrated titanium oxides [8, 15, 28, 33, 34]; hydrated chromium oxides [5, 10, 18, 23-25];

hydrated iron oxides [7, 17, 20, 23, 29]; hydrated zirconium oxide [26]; hydrated tin oxide [31]; hydrated thorium oxides [8].

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Aluminum Hydroxide Gel

α-GEL BY THE METHOD OF WILLSTÄTTER AND KRAUT

$$Al(OC_2H_5)_3 + 3H_2O = Al(OH)_3 + 3C_2H_5OH$$

In the method of Schmäh [25], 400 ml of CO_2-free double-distilled water is placed in a one-liter, three-neck flask, whose center neck carries a mercury-seal stirrer. One side neck is closed off with a soda lime tube. The other is fitted with a dropping funnel with an ungreased stopcock from which a solution of 3 g. of aluminum ethoxide in 200 ml. of absolute ethanol is allowed to run in a thin stream into the vigorously stirred water (the aluminum ethoxide is prepared from Si- and Fe-free 99.99% Al by one of the methods given on page 840 and is then dissolved by refluxing with the required amount of ethanol). During the hydrolysis of the ethoxide, the temperature rises by 6-8°. The precipitate is washed by decantation with double-distilled water (the settling may be speeded up by centrifugation).

PROPERTIES:

The α-gel is completely free of electrolytes; its surface is quite alkaline. The fresh gel is completely amorphous [19]; it ages rapidly to bayerite via the intermediate stage of böhmite, the alkalinity of the surface decreasing considerably in the process [16, 17]. Aluminum oxides prepared from this gel are more active than the usual aluminum oxide catalysts [1].

GENERAL:

This method of preparation allows some latitude in the hydrolysis conditions as well as in the alcohol moiety of the alkoxide. The hydrolysis may be carried out in absolute ethanol

solution, the hydrolysis agent being atmospheric moisture (stirring in air). Alternatively, aqueous alcohol may be added to the ethanol solution, or the hydrolysis may be carried out in the reverse fashion, by addition of the alcoholic solution to water (the water may be hot, if required). Ammonia solution may be used instead of water. Solid alkoxides (such as some methoxides) may be hydrolyzed in a stream of moist air with heating if required [27]. Since the hydrolysis of alkoxides of metals of variable valence may proceed in steps [2, 5, 11], the most active products are obtained on fast precipitation.

The ability of the alkoxide to undergo hydrolysis depends on the nature of the alcohol moiety. This ability decreases with increase in the molecular weight of the organic part and increases in the order of primary to tertiary alcohol (as shown by zirconium and titanium alkoxides [6, 8, 26]). The volatility of the alkoxides increases in the same order. This fact is of some importance, because with elements having a high atomic number, it is often only the tert-alkoxides that can be distilled (and thus purified), even in high vacuum (for example, Th [10]).

A high hydrolysis temperature accelerates the aging process, so much so that in some cases the amorphous hydrated oxide cannot be isolated.

The following references deal with metal alkoxides:

DropBooks

Metal	Method of preparation of the alkoxide	Hydrolysis and products of hydrolysis
Al	p. 840 this handbook	[1, 3, 16, 17, 19, 21, 25]
Si	[7], see p. 702	[2, 18, 22, 32], see p. 698
Ti	[4, 7, 11, 24, 26, 27]	[5, 11, 15, 18, 20, 23, 26, 27]
Cr	[30]	[30]
Fe	[24, 28, 29]	[29]
Zr	[6–8, 24]	[6]
Nb	[14]	
Sn	[24, 31]	[31]
Ce	[13]	
Hf	[9]	
Ta	[12]	
Th	[10, 13]	

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"Glimmering" Hydrated Iron (III) Oxide

In the method of Kohlschütter et al. [3], 20 g. of $FeSO_4 \cdot 7\,H_2O$ (analytical grade) is boiled for 40–60 minutes in a Kjeldahl flask

with 200 ml. of pure 70% H_2SO_4. The water vapor is allowed to escape in order to concentrate the acid. Following the reaction the tablet-shaped crystals (which range in size up to 2 mm.) are collected on a fritted-glass filter. They are washed with some water, then several times with acetone, and are then dried in vacuum. The dry crystals are reacted (vigorous stirring) with 200 ml. of 2N aqueous ammonia (or correspondingly less of a more concentrated solution). The reaction is over in 10-15 minutes. The product is allowed to settle, the mother liquor is decanted, and the residue washed 4-5 times by decantation with water. The hydrated oxide is collected on a filter, rinsed several times with water, and dried with acetone and ether.

To obtain a preparation with a particularly impressive glimmer, the substance is predried with ether (as above) and then carefully heated at 300°C for 30 minutes.

PROPERTIES:

Contains, even after baking at high temperature, a considerable amount of water. Single, freely flowing particles retaining the external shape of sulfate crystals. Amorphous on x-ray analysis; the hydroxide framework is permeated by numerous pores. Crystallizes spontaneously and with glowing to α-Fe_2O_3 on heating to 350°C.

DropBooks

GENERAL:

The ability of the system to undergo a topochemical reaction depends on several prerequisites: the solid should not dissolve too rapidly (otherwise the reaction does not occur at the interface but in solution). This prerequisite is often fulfilled by sulfates of trivalent metals. If necessary, the rate of solution may be reduced by adding a sufficient quantity of an organic substance to the aqueous solution. The organic substance may be acetone, glycol, glycerol, dioxane and so forth, or in the case of hydroxide "precipitations," it may be pyridine, mono-, di- or triethanolamine, morpholine and so forth (see [6]).

The reaction product, which is formed on the surface of the reacting crystals, should not form a solid film: it must be permeable to all reagents present in solution so as to allow the completion of the reaction throughout the individual crystallites.

Instead of simple salts, one can use double salts with readily soluble components. Thus, $KAl(SO_4)_2 \cdot 12\,H_2O$ yields a granular hydrated aluminum oxide with a very porous structure [6]. Basic salts may also be reacted topochemically to yield hydrated oxides.

The "glimmering" was also observed in hydrated oxides of Cr, Ti, Zr [1, 10], Sc, Nb, Ta [10] and others.

Another topochemical method for preparation of hydrated oxides consists of an extension of the procedure proposed by Raney in the case of metals. The required starting mixtures may be obtained by fusion of the components or by coprecipitation. A commercial fusion procedure yields Vycor glasses with interesting adsorptive and catalytic properties [4, 5, 9]. The fusion procedure is also used to obtain sodium ferrite–aluminate mixed crystals; these then yield hydrated iron (III) oxide skeletal structures showing considerable chemical activity (reacting with hot aqueous NaOH) provided the starting mixture contains an excess of aluminate [7]. The activity of such structures is due both to the small particle size of the product and to a strongly distorted crystal lattice due to "frozen" thermal vibrations [8].

Coprecipitation of silicic acid with hydrated oxides of metals such as Fe, Al, Cr, Ca, Cu, Ni and so forth yields silica gels that, after washing, drying and activation by leaching with hydrochloric acid, give chalky materials (provided the metal concentration in the starting mixtures is high [2]).

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ACTIVE METAL OXIDES

The methods of preparing active metal oxides may be grouped according to similarities of procedure or of structure of the product.

PREPARATION BY TOPOCHEMICAL REACTIONS

The topochemical reactions that give activated oxides are essentially thermal decompositions of suitable compounds:

1) Dehydration of hydroxides [see aluminum oxide, p. 1660; α-iron (III) oxide, p. 1661].

2) Thermal decomposition of nitrates, carbonates, oxalates and so forth (see magnesium oxide, p. 1663; zinc oxide, p. 1664).

3) Dehydration of hydrated oxides in the mother liquor [see lead (IV) oxide, p. 1668].

The products prepared under mild conditions are usually (porous) pseudomorphs of the particles of the starting material (see [17]). Reproducible preparation of active oxides requires not only constant decomposition conditions, but also consistently uniform starting materials (constant conditions during precipitation and so forth). The effects of the chemical composition and the physical structure of the starting material on the properties of the final product decreases with increasing decomposition temperature. The extent of this decrease is proportional to the extent of ageing of the products during reaction conditions.

Kinetic measurements on thermal decomposition reactions yield several empirical equations. In general, these may be interpreted as follows:

1. If the order of the reaction is 1/3, the process is diffusion-controlled.

2. If the order of the reaction is 2/3, the process is a decomposition reaction which progresses from the outside to the center.

If the specific surfaces of the products are plotted against the decomposition temperature (at constant decomposition time), typical curves are obtained [3]. From these, once can not only read off the optimum conditions for creation of maximum surface but one can also obtain some indication of the mechanism of the decomposition reaction. Complete explanation of these phase relations (in some cases, an extremely complicated problem) requires the use of x-ray and IR spectroscopy and thermogravimetric methods.

In practice the decomposition temperature must be exactly maintained. Thus one cannot employ a shorter reaction time at higher temperature without incurring a loss of activity in the material. The effect of the atmosphere in which the reaction proceeds is especially remarkable. In some cases it was possible to reduce the activation energies for the decomposition by 10-15 kcal./mole (by comparison with those needed in air or vacuum) by proper choice of the gaseous atmosphere. In many cases, a properly chosen gaseous atmosphere allows the decomposition to proceed at unusually low temperatures; this in turn gives high active preparations [2].

PREPARATION BY CONDENSATION FROM A HOMOGENEOUS PHASE

The only oxides that can be condensed from the gas phase are those that are vaporized products of a chemical reaction occurring immediately prior to the condensation. Otherwise,

vaporization of oxides is usually impossible due to the high boiling points involved.

Colloidal suspensions of oxides in air (smokes, see p. 1669) usually are very nonuniform because of the randomness of nuclei formation [1, 6]. The individual particles are usually globular. The growth of particles from the gas phase occurs in two stages:

Primary growth, which is exceedingly rapid and produces particles 500-1000 A in diameter. In this stage, the only material condensed is that which finds itself within the confines of a "sphere of influence" of a nucleus.

Secondary growth, which is much slower and depends mainly on the vapor pressure of the material under the temperature conditions prevailing during growth. This stage, corresponding to the aging of precipitates under mother liquors, can be suppressed by quenching of the material.

PREPARATION BY INTERFACE REACTIONS

Under some conditions, the texture of oxide growth layers is determined by epitaxy with the support. Such layers are obtained by:

1) Surface oxidation of metals and alloys (e.g., bluing layers by heat treatment).

2) Oxidation of metal layers deposited electrolytically or from a vapor on carriers other than the metal itself. Occasionally, such surface layers show oxide modifications which are not known to occur in the pure material. In some metals the colored layers formed by strong oxidation are covered with needles or leaflets of the oxide [9]. The dimensions of these depend on the duration and the temperature of the oxidation. The rough surface thus produced may sometimes offer twice the normal specific surface [11].

Because these processes are related to catalysis, they have recently been studied by many investigators. This is especially true of the initiation reaction and the process kinetics [5, 7].

In view of the enormous complexity of the subject, the methods for the preparation of mixed and carrier-supported oxide catalysts can only be summarized here. They include:

1. Mechanical mixing (dry, in an atmosphere laden with moisture, under special gases, in suspension, and so forth [10]).

2. Coprecipitation, especially when solids of definite composition are desired; it is also applicable to the more rarely used solid solutions.

3. Precipitation of one component onto a carrier which is itself suspended in solution.

4. Adsorption of ions of one component from a solution and so forth [8].

The interaction of the components of a mixed catalyst (promotion of catalytic activity), which in general requires thermal activiation for development of the full effect, is a very complex process; occasionally, it yields very active and very specific catalysts.

The two special effects accompanying such an interaction are:

1. Alteration of the semiconductor properties of an oxide by inclusion of other oxides with different valences in the crystal lattice [5, 16]; this may also alter the activation energy of a catalytic process [14].

2. Adaptation of valence. The metal in the precipitated oxides of some transition metals adapts to the valence of the metal in the oxide carrier. Thus, transition metals preferably deposit on MgO in divalent forms while on γ-Al_2O_3 they are trivalent and on TiO_2 (rutile) tetravalent [15]. This is because the oxide precipitate attempts to continue the crystal lattice of the carrier.

Various methods are available for shaping the oxide catalysts [4]. The following methods are used in laboratories:

The material, which may be moist if required, is pressed into a sheet. After drying, it is broken up and sieved. However, the high pressure applied during sheet forming produces a large decrease in the average pore size. This may lead to a considerable reduction of the catalytic activity of such preparation, especially at large reagent throughputs (the diffusion, which controls the overall process rate, becomes hindered by the small pore size [12]).

In the second method the dry powder is made into a paste with 80% ethanol. The paste is then rolled (without applying any high pressure) into a thin sheet, which is then forced through a polished copper or nickel screen of suitable mesh size (1-2 mm.). After drying, the granulated material may be scraped off from the reverse side of the screen. If the dilute ethanol does not yield stable granules, the paste may be made with a saturated aqueous solution of the corresponding metal nitrate. In this case, the granules are shaped as above, dried and baked at 200-220°C until nitrous fumes cease to evolve [13].

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Aluminum Oxide

Depending on the conditions, certain aluminum hydroxides yield active γ-oxides on thermal decomposition. These possess interesting adsorptive and catalytic properties.

I. ADSORBING AGENT

$$\underset{156.0}{2\,Al(OH)_3} = \underset{101.9}{Al_2O_3} + 3\,H_2O$$

An aluminum oxide which is especially suitable for use as an adsorbing agent is obtained by heating aluminum hydroxide gel (see p. 1652) or hydrargillite (see p. 820; for preparation of an almost completely alkali-free material, see [18]) for several hours at 250-300°C. The heating proceeds in vacuum or in a stream of dry gas, and is continued until the concentration of the water has bound in the crystals decreases to 6-8 wt. %.

PROPERTIES:

Fine, white powder which flows like sand; specific surface: 250-300 m.²/g. [26]. The powder pattern shown böhmite lines, although the water content differs significantly from that of böhmite (15.02%). The thermodynamic potential, amounting to several kcal./mole, is due to the large surface and the defect lattice [27].

II. CATALYSTS

Aluminum oxide catalysts are prepared by heating hydrargillite at 550-650°C (other aluminum oxides give less active preparations); the content of water of crystallization is 1% or slightly less.

PROPERTIES:

Hygroscopic powder, very similar in appearance to the above-described adsorption agent. The particles show a honeycomb-like secondary structure; the preparations show very uniform powder patterns (according to Glemser [17], they consist of ϵ-phase). Any water adsorbed during use is incorporated in the form of OH groups and thus causes rehydration [18].

α-Iron (III) Oxide

For chromatographic adsorption

In the method of Glemser and Rieck [19] a solution of 1000 g. of $Fe(NO_3)_3 \cdot 9\ H_2O$ (A.R. or pure) in 2.4 liters of water is added with constant stirring to 2.4 liters of 6% aqueous ammonia. The precipitate is centrifuged off and washed with water until the wash liquor is free of nitrates. It is then dried at 50°C. After two days at this temperature it is broken up and freed of dust on a U.S. 400 standard screen. Long heating (10–16 hours) of this crude product at high temperatures gives preparations with other activities. The maximum activity is usually reached by heating at 180–220°C for 10 hours.

DropBooks

GENERAL:

The rate of dehydration of hydroxides and hydrated oxides may be varied within limits by choice of suitable experimental conditions. Aside from the obvious effect of temperature, the following dehydration procedures are open to the experimenter and give better products than does simple heating in open dishes or crucibles:

1. Removal of the water by means of a dry stream of air or other gas. The dehydrating action of the various gases is quite specific; hydrogen is an especially efficient dehydrating gas [25].

2. Reduction of the vapor pressure of water in the atmosphere surrounding the solid by operating under vacuum or using drying agents. If a drying agent is used, the material may be placed in a drying pistol instead of a desiccator. In this case, the sample may be heated to a high temperature while cooling the drying agent. This produces a large water vapor pressure gradient. It should be remembered that the pressure of water in equilibrium with active oxides is much lower than that encountered in equilibrium with inactive materials. In many cases it is impossible to obtain completely dry oxides without reducing the activity to a level considerably below the maximum.

One remarkable phenomenon, which has been proved over and over again, is the fact that dehydrations of the above type do not alter the shape and size of secondary particles, while the size of the primary particles is subject to sharp variations [29].

Dehydration in hydroxides and hydrated oxides is often quite sensitive to impurities [1]. To obtain reproducible results, one should always use starting materials of the same purity.

Literature references for the preparation of active metal oxides by dehydration of hydroxides:

Oxide	Starting material	References
BeO	α-$Be(OH)_2$ (see p. 894)	[9]
MgO	$Mg(OH)_2$ (see p. 912)	[10, 23]
γ-Al_2O_3	$Al(OH)_3$, amorphous (see p. 1652)	[24, 26]
	$Al(OH)_3$, hydrargillite (see p. 820)	[2, 18, 20, 26, 27]
	$Al(OH)_3$, bayerite (see p. 821)	[4, 18, 20, 27]
	AlOOH, böhmite (see p. 821)	[12, 13, 18, 26, 27, 29]
TiO_2	Hydrated titanium (IV) oxide	[21]
Cr_2O_3	Hydrated chromium (III) oxide, amorphous (see p. 1648)	[3, 25]
α-Fe_2O_3	Hydrated iron (III) oxide, amorphous	[6, 8, 14, 19, 22]
	α-FeOOH (see p. 1499)	[6]
γ-Fe_2O_3	γ-FeOOH (see p. 1500)	[15, 16]
NiO	$Ni(OH)_2$ (see p. 1549)	[28]
ZnO	ϵ-$Zn(OH)_2$ (see p. 1074)	[5]
	Other crystalline hydroxides	[11]
CdO	$Cd(OH)_2$ (see p. 1097)	[7]

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Magnesium Oxide

Active MgO is prepared by calcination of the basic carbonate (for preparation, see p. 911). The following particle sizes have been observed, depending on the temperature and the duration of the calcination, [12]:

Temp., °C	Heating time, hr.	Particle size in A	
		Determined by x-ray analysis	Observed by ultramicroscope
670	60	30	100
725	1—4	46	100
820	1—4	50	100
920	1—4	300	200— 300
980	1—4	300	300— 500
1200	4	300	1000—3000

Since commercial basic magnesium carbonates are not well-defined compounds, the properties of the oxides vary to some extent. To obtain preparations with reproducible properties it is better start with well-defined compounds such as fine crystalline $Mg(OH)_2$ (for preparation, see p. 912) or with $MgCO_3 \cdot 3\ H_2O$ [3, 22].

Zinc Oxide

$$\underset{189.4}{ZnC_2O_4 \cdot 2\,H_2O} = \underset{153.4}{ZnC_2O_4} + 2\,H_2O$$

$$\underset{153.4}{ZnC_2O_4} = \underset{81.4}{ZnO} + CO_2 + CO$$

A solution of 27.3 g. of anhydrous $ZnCl_2$ is in 200 ml. of water and 2.5 ml. of 2N HCl is prepared. Another solution, containing 31.3 g. of $(NH_4)_2C_2O_4 \cdot H_2O$ in 2.0 ml. of water and 2.5 ml. of 2N aqueous NH_3 solution, is prepared separately. Both solutions are heated to 70°C, and the oxalate solution is then poured in a thin stream into the vigorously stirred zinc salt solution. The oxalate precipitate is washed by decantation with water until it is free of chlorides. It is then placed on a filter and dried by suction. The $ZnC_2O_4 \cdot 2\ H_2O$ is then transferred to a flat pan which is placed in a drying oven. The temperature is then raised to 240°C over a period of 6 hours and is then maintained at this level for an additional 12 hours. This treatment removes nearly all of the water of crystallization. The anhydrous oxalate is then converted to ZnO by heating at 400°C for 4 hours.

PROPERTIES:

Fine, white powder; untamped bulk density (pouring into a cylinder) 0.85 g./ml. The primary particles, whose lattice still contains defects, are larger than 500 A [18].

GENERAL:

Oxides of metals exhibiting low basicity may be obtained by thermal decomposition of their salts with volatile or readily decomposed acids. Such salts include nitrates, carbonates, formates and oxalates. In order to obtain active preparations, the decomposition conditions should be as mild as possible. The decomposition proceeds faster in vacuum than in air, so that the reaction temperature may be lower (for the same yield per unit time). An even stronger influence on the reaction rate is sometimes exerted by an appropriate gaseous atmosphere (see below).

NITRATES

Hydrates of most heavy metal nitrates have low melting points. Thus, on heating, they liquefy, decompose and leave sintered or foamed oxides of low surface area. The product may sometimes be improved by starting with lower hydrates or basic nitrates. Nitrate decomposition is important primarily in the production of carrier substances.

In compounds possessing several oxidation stages (e.g., elements of the manganese series), nitrate decomposition always yields the highest oxide possible at the given reaction temperature.

CARBONATES

Vacuum decomposition of carbonates is often used to obtain metal oxides where the metal is at the oxidation stage corresponding to that in the starting carbonate. However, with air present, at least partial oxidation is possible, sometimes even after the material has been cooled to room temperature. In addition to carbonates and their hydrates, as well as basic carbonates, this method is suitable for the decomposition of double carbonates where ammonium is one of the cations [for example, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4\,H_2O$]. When the conditions are mild, very fine oxide powders are frequently obtained.

The decomposition of magnesite has been studied very thoroughly and proves to follow 2/3 order kinetics (see p. 1657 and [17, 21]). The effect of a gaseous atmosphere on the kinetics of this reaction consists mainly in the change in the activation energy for decomposition which it causes [8, 9].

Atmosphere	Dry air	Vacuum	H_2	Moist air	H_2O
Activation energy in kcal./mole	42.15	36.13	27.89	27.22	26.79

The preparative decomposition of magnesite may be carried out even at 500°C when a suitable atmosphere, e.g., air containing H_2O and NH_3 at a total partial pressure of 40 mm., is provided [19]. The gaseous atmosphere over the preparation also affects the particle size of the nascent solid phase. Thus, given identical decomposition temperatures, the particle size of MgO crystals formed from magnesite will decrease with decrease of the CO_2 pressure during the decomposition [10].

FORMATES AND OXALATES

The nature of the thermal decomposition of formates and oxalates is not uniformly the same. Depending on the basicity of

the metal and the degree to which it approaches the noble metals, one may obtain carbonates, oxides or the metals themselves, provided secondary oxidation reactions are prevented (the production of metals is due to reduction by the organic anions or their decomposition products). According to presently available data, formates and oxalates behave in this respect in practically identical fashion. As far as is known, the composition of products obtained on vacuum decomposition is identical to that of the primary products of decomposition in air. The following data are available on some of the divalent metals:

Formate or oxalate of	Decomposition products in vacuum and primary products of decomposition in air	Terminal products of decomposition in air
Mg*	MgO	MgO
Mn	MnO	Higher oxides
Fe	FeO	α- and γ-Fe_2O_3
Co	Co	Higher oxides
Ni	Ni	NiO_{1+x}
Cu	Cu	CuO
Zn	ZnO	ZnO

*At the mild decomposition temperatures assumed in this table, the salts of the heavier alkaline earths always produce carbonates.

Under certain decomposition conditions, Cd and Pb (II) oxalates give a mixture of oxide and metal [6, 11, 15]. In contrast to the corresponding formates, the oxalates of the metals mentioned here are rather insoluble in water; in general, they are readily obtained by precipitation, which usually gives a fine powder well suited as a starting material for decomposition. Provided the solvent is cautiously removed, hydrated or solvated compounds also yield suitable starting materials, and decomposition of these gives products with high activities.

Ultramicroscopic and x-ray studies show that oxides obtained from carbonates and oxalates at low decomposition temperatures are pseudomorphous with the crystals of the starting material [10, 12]. Since the molar volume of the new substance is as a rule considerably smaller than that of the starting material, the particles of the product are usually very porous, that is, provided the reduced decomposition temperature $T/T_m < 1/3$ (compare p. 1611). If the decomposition temperature is higher, aggregate crystallization can be expected to an increasing degree [19], except when the starting substance (which must in this case be a uniform fine powder) is heated for such a short time that only the desired

reaction occurs and no time is left for the material to undergo aggregation [20]. Fast cooling from the decomposition temperature may help in this case.

The following are literature references for the preparation of active oxides by thermal decomposition of suitable compounds:

Preparation	Formation from			
	Nitrate	Carbonate	Formate	Oxalate
BeO		See p. 893		
MgO		[3, 7, 22]	[25]	[16, 23]
Mn oxides	[9]; see p. 1458	See p. 1456	[25]	[23]; see p. 1456
Fe oxides			[5]	[5, 23]; see p. 1497
Co oxides		See p. 1519	[25]	[23]
Ni oxides	[14, 26]; see p. 1548	[14, 24]; see p. 1548	[25]	[1, 23]
CuO	[24]; see p. 1012		[25]	
ZnO	[18]	[18, 27]	[25]	[18, 23]
CdO			[25]	[11, 15]
ThO_2	See p. 1221			[2, 13]; see p. 1221

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Lead (IV) Oxide

$$\underset{443.4}{Pb(CH_3COO)_4} + 2H_2O = \underset{239.2}{PbO_2} + 4CH_3COOH$$

The instructions given on p. 767 are used to prepare 50 g. of $Pb(CH_3COO)_4$. The material is then crushed and triturated with 460 ml. of water in centrifuge tubes until all tetraacetate is converted to brown PbO_2. The fine suspension is then centrifuged. The deposit is stirred four times with water (500 ml. each time); the suspension is centrifuged each time before decanting the liquid. The last wash water should not be acid. The PbO_2 is then suspended in 50 ml. of water, filtered with suction, and washed on the filter with 50 ml. of water. Then the material is washed on the funnel with four 25-ml. portions of acetone to displace the water. The acetone is then displaced by washing with four 25-ml. portions of ether. This imparts the final color to the material. The product is immediately placed in a vacuum desiccator [5].

PROPERTIES:

Very fine, dense powder with a light brown, coffeelike color; reacts with dil. HCl to give chlorine. Its physical state, characterized by small particle size, lattice defects and occlusions of admixtures which prove to be amorphous and on x-ray analysis are recognizable under an ultramicroscope [6], causes an extraordinary high chemical activity. Especially useful in dehydrogenation of aromatic dihydroxy compounds to the corresponding

quinones. Pure preparations age with release of O_2, losing their activity (5% in 15 hours, 8-11% in 7 days).

GENERAL:

Spontaneous dehydration of hydroxides is occasionally also observed in precipitations with alkali hydroxide solutions. The method is especially useful in preparation of CuO [2, 7], ZnO [3] and Ag_2O [4]. The products thus obtained are usually fine powders and quite frequently contain occluded admixtures which prove amorphous on x-ray analysis. The rate of dehydration depends on the particle size of the precipitated hydroxide and on the possible formation of intermediate basic salts. The latter may inhibit the dehydration to a considerable extent. An especially useful starting material for preparation of CuO is $Cu(NO_3)_2$ [1].

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Colloidal Suspensions of Oxides in Gases (Smokes)

Oxides of especially small particle size (smokes) may be obtained under appropriate reaction conditions. Such reactions are nearly always described in conjunction with special investigations where only very small amounts of compound are necessary. Only occasional literature references to work on a preparative scale are available. However, these may be supplemented by data and descriptions from the patent literature, since oxide smokes are prepared on an industrial scale. The following methods are the most useful for generation of oxide smokes:

1) **Burning of the metal** (e.g., Mg, Zn, Cd and so forth); however, this procedure frequently converts only part of the oxide to the desired colloidal (smoke) dispersion.

2) **Oxidation of a metal volatilized in an electric arc.** This simple method is frequently used to demonstrate the present phenomenon. The procedure consists of striking an arc between

two electrodes made of the desired metal. However, it is only rarely useful for preparative purposes, since the quantity of product is very small due to the high thermal conductivity of the electrodes and the frequent shifts in the arc focus.

A much higher efficiency is reached in the apparatus developed by V. Kohlschütter [5] (see Fig. 340), comprising an arc furnace with vertical electrodes. The bottom electrode has an indentation for the metal to be volatilized. The arc is struck between the metal and the top (movable) electrode. Usually the vaporization proceeds very smoothly if the metal is the anode. The optimum conditions for the operation of the arc and for removal of the vapors from the electrodes vary somewhat from metal to metal.

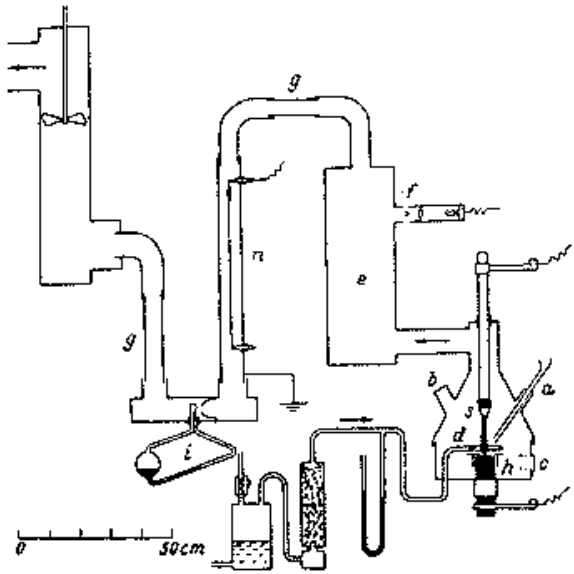

Fig. 340. Preparation of active metal oxides by oxidation of metal vapor. *a* funnel for addition of metal; *b* observation port; *c* side port; *d* circular nozzle for air intake; *e* first chamber with lateral observation ports (these are not shown); *f* illuminating device; *g* glass tubes (the remaining parts of the apparatus are made from sheet iron); *h* carbon electrodes; *i* flow meter activated by differential pressure; *n* precipitation cell; *s* movable carbon electrode.

3) Thermal or photochemical decomposition of volatilized **metal compounds in the presence of oxygen.** Metal compounds that

are usable in such reactions are carbonyls and certain metal hydrides or organometallic compounds, for example, alkylated metals. To avoid explosions, the reaction must be carried out at very low pressures or the partial pressure of the reagents must be reduced by appropriate dilution with an inert gas. The reactions may be carried out either in closed systems [4, 10] or in a gas stream [11]. The continuous apparatus is shown in Fig. 338.

The decomposition of $Fe(CO)_5$ has been investigated very thoroughly. It was found that it oxidizes according to the following equation:

$$\underset{736.6}{4\ Fe(CO)_5} \xrightarrow{(O_2)} \underset{319.4}{2\ Fe_2O_3} + xCO_2 + yCO$$

Low O_2 concentrations in the starting mixture, high temperatures and short reaction times give thoroughly crystalline γ-Fe_2O_3; this material gives sharp powder patterns. Lower decomposition temperatures and higher oxygen partial pressures produce smaller smoke particles; however, the particles show powder patterns which are less distinct [11]. Similar investigations have also been carried out on the decomposition of $Pb(CH_3)_4$ [6].

4) Decomposition of halide vapors. Readily vaporized halides, especially the chlorides of elements such as Al, Si, Ti, Zr, Sn and so forth, may also be converted to oxides in the gas phase. This may be done in either of the following ways:

a) Saturation of a stream of an inert gas with the chloride, followed by reaction with steam. External heating is required in this case.

b) Combustion of the chloride together with hydrogen or with a combustible gas which contains bound hydrogen, e.g.:

$$\underset{339.8}{2\ SiCl_4} + \underset{32.1}{2\ CH_4} \xrightarrow{(O_2)} \underset{120.1}{2\ SiO_2} + 8\ HCl + xCO_2 + yCO$$

The second gas may be preheated or the combustion mixture may be diluted with an inert gas (to avoid excessive temperatures), depending on circumstances.

Under suitable reaction conditions this procedure yields extremely fine oxide powders which are used industrially as active, white fillers [2, 7].

Some difficulties in the preparation of oxide smokes arise in the separation and collection of the smoke particles. The apparatus of Kohlschütter solves the problem partially by using a dust collector and a Cottrell precipitator. However, losses are still heavy due to elutriation of the smallest particles.

The following are literature references for the preparation of oxide smokes from metals or carbonyls:

Oxide	MgO	Al_2O_3	Cr_2O_3	Fe_2O_3	NiO	CuO	ZnO	CdO	SnO_2	PbO	Bi_2O_3
from metal	[1]	[5]	[5]	[1, 9]	[1, 5]	[5]	[1, 5]	[1, 3, 5]	[5]	[5]	[5]
from carbonyl				[1, 4, 8, 10, 11]							

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Copper-Chromium Oxide

$$\underset{252.1}{(NH_4)_2Cr_2O_7} + \underset{68.1}{4\,NH_3} + 3\,H_2O + \underset{(3\,H_2O)\ 483.3}{2\,Cu(NO_3)_2} = \underset{429.3}{2\,Cu(OH)NH_4CrO_4} + 4\,NH_4NO_3$$

$$\underset{429.3}{2\,Cu(OH)NH_4CrO_4} = \underset{79.6}{CuO} + \underset{231.6}{CuCr_2O_4} + 5\,H_2O + N_2$$

A solution of 126 g. of $(NH_4)_2Cr_2O_7$ A.R. in 600 ml. of water is prepared, and 150 ml. of 28% aqueous ammonia is added to it. This solution is poured in a thin stream into a warm (50–60 °C) solution of 242 g. of $Cu(NO_3)_2 \cdot 3\,H_2O$ in 800 ml. of water while stirring manually. The reddish-brown precipitate of $Cu(OH)NH_4CrO_4$ [3] is stirred for an additional few minutes and then filtered on a Büchner funnel. The moisture is pressed out and the filter cake dried in an oven at 110°C. The mass is then broken up into coarse pieces and heated in a covered nickel or porcelain dish in a muffle

furnace (350–450°C, one hour). The product ($CuO + CuCr_2O_4$) [10, 11] is ground in a mortar and suspended three times in 10% acetic acid (1.2 liters each time); the product is settled and the liquid decanted after each washing. This removes the CuO. The residue is washed four times with water in the same manner, filtered with suction, dried at 110°C and ground. After the last washing the precipitate sometimes settles only with difficulty due to partial peptization [8].

After this treatment, the catalyst may still contain an excess of CuO; the latter may convert during use to Cu_2O [9], which decreases the catalytic activity. The deactivation of the catalyst is much less likely if 24 g. of the $Cu(NO_3)_2 \cdot 3\,H_2O$ in the initial charge is replaced by 26 g. of $Ba(NO_3)_2$. The Ba appears in the product catalyst as $BaCrO_4$ [11]. Equivalent quantities of Mg, Ca, Mn (II) or Zn nitrates may be used instead of the $Ba(NO_3)_2$.

PROPERTIES:

Fine black powder; completely stable in atmospheric oxygen and moisture. Active catalyst for the hydrogenation of organic hetero compounds containing multiple bonds [1, 5].

GENERAL:

Even the simple ammonium chromates can undergo thermal decomposition [4, 6, 7, 12] which yields very active Cr (III) oxides on decomposition in the air. Partial formation of higher chromium oxides is observed at reduced pressures [6]. Since these decomposition reactions release a considerable quantity of heat, they must be carried out in thin layers (flat dishes); the mildest conditions are obtained if only one spot in the dish is heated at a time and that spot is pushed onto a cold surface as soon as the material starts to react. The thermal decomposition of NH_4MnO_4 in air leads to explosions; vacuum decomposition yields, apart from NH_4NO_3, manganese oxides [Mn (III)–Mn (IV)], which are pseudomorphous to the starting crystals [2].

The above method is also useful for the production of other mixed oxides where chromium oxide is a constituent, e.g., Mn–Cr oxide, Zn–Cr oxide [13].

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Hopkalite (Hopcalite)

HOPKALITE I

Hopkalite I is a mixture of 50% MnO, 30% CuO, 15% Co_2O_3 and 5% Ag_2O [9]. Its constituents are prepared as follows:

a) Manganese dioxide [2, 5]

$$\underset{316.1}{2\,KMnO_4} + 5\,H_2SO_4 = K_2SO_4 + 2\,Mn(SO_4)_2 + 5\,H_2O + 1^1/_2\,O_2$$

$$2\,Mn(SO_4)_2 + 4\,H_2O = \underset{173.9}{2\,MnO_2} + 4\,H_2SO_4$$

Cold 75% sulfuric acid (650 g.) is poured over 100 g. of fine $KMnO_4$ powder; the mixture is left standing for several days. During this time, the initially separating $HMnO_4$ decomposes with evolution of oxygen, leaving a dark yellow Mn (IV) solution. This is added to a large excess of water; a very fine powder of hydrated MnO_2 separates out. This powder is washed several times by decantation with water. The washing is continued on a funnel until the filtrate is free of sulfate.

Alternate method: Reduction of permanganate by Mn (II) salts [1, 4, 13].

b) Copper oxide [9] (see also [6]):

$$\underset{(5H_2O)}{\underset{249.7}{CuSO_4}} + \underset{80.0}{2\,NaOH} = \underset{79.6}{CuO} + Na_2SO_4 + H_2O$$

A solution of 103.5 g. of $CuSO_4 \cdot 5\,H_2O$ in 300 ml. of water is poured with efficient stirring into 430 ml. of 2N NaOH preheated to about 80°C. The mixture is stirred for a few minutes; during

this time, 2N H_2SO_4 is added until the solution, which contains the CuO in suspension, becomes neutral (about 15 ml. of the acid is required). The mixture is allowed to settle and washed in the same way as the MnO_2 (see above).

c) Cobalt (III) oxide [8]

$$\underset{(7\,H_2O)\ 562.2}{2\,CoSO_4} + \underset{160.0}{4\,NaOH} + NaOCl = \underset{165.9}{Co_2O_3} + 2\,Na_2SO_4 + NaCl$$

A solution of 56.2 g. of $CoSO_4 \cdot 7\,H_2O$ in 200 ml. of water is mixed at room temperature with a slight excess of strongly alkaline hypochlorite solution. As soon as gas evolution comes to a virtual stop, the solution is decanted from the immediately appearing dense black precipitate, which catalyzes the decomposition of excess hypochlorite. The washing procedure is the same as for MnO_2.

The oxides prepared as in (a), (b) and (c) are suspended in about 1.5 liters of water. This suspension is then mixed with a solution of 8.07 g. of $AgNO_3$ in the minimum amount of water, and the Ag_2O is precipitated by addition of 23.8 ml. of 2N NaOH (intensive stirring). Further treatment is given under Hopkalite II.

DropBooks

HOPKALITE II

Hopkalite II consists of 60% MnO_2 and 40% CuO (the MnO_2:CuO molar ratio is 1.375). The catalyst may be prepared by mixing the separately prepared components [10] or by mixed precipitation ([13]; see also [11]).

a) $$\underset{(4\,H_2O)\ 223.1}{MnSO_4} + \underset{80.0}{2\,NaOH} + {}^1/_2\,O_2 = \underset{86.9}{MnO_2} + Na_2SO_4 + H_2O \qquad [4]$$

b) $$\underset{(5\,H_2O)\ 249.1}{CuSO_4} + \underset{80.0}{2\,NaOH} = \underset{79.6}{CuO} + Na_2SO_4 + H_2O$$

The reactor is a three-liter Erlenmeyer flask, in which 155 g. of $MnSO_4 \cdot 4\,H_2O$ and 125 g. of $CuSO_4 \cdot 5\,H_2O$ are dissolved in 1.5 liters of hot (70–80°C) water. A fast stream of air is then bubbled through the hot solution and 400 ml. of 25% NaOH is added (vigorous shaking) from a dropping funnel. The passage of air is continued for another 10 minutes. The precipitate is then washed several times by decantation with hot water. Then washing is continued on a filter until the wash liquor is neutral. The precipitate is suction-dried (the water should be removed as completely as possible by repeated pressing). After the by-product fine powder

has been sieved out, the product is granulated by heating for 3 hours at 200°C.

PROPERTIES:

Brownish-black granules, which must be stored under anhydrous conditions. Catalyzes the combustion of CO at room temperature; used in gas-mask cartridges.

GENERAL:

The methods of preparation described above consist of precipitation immediately followed by a reaction of the precipitated product (dehydration, oxidation). The oxidation is a topochemical reaction yielding products with defect structures. The full activity of such a multiple-compound catalyst can frequently be developed only after an aging process called forming. To strengthen the structure of the catalyst granules (which at the same time increases the accessibility of their internal surfaces to gases), rather large amounts (up to 50% and more) of kieselgur may be added to the catalyst (as, for instance, in the Fischer-Tropsch catalysts).

Some other oxidation catalysts based on metal oxides have been described in the literature: Ag_2O-Cu_2O [7]; Ag_2O-Cr_2O_3 [12] and MnO_2-CuO-Co_xO_y [3].

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SECTION 2

Hydroxo Salts

R. SCHOLDER

General

"Hydroxo salt" is the term used for a group of complexes where the central atom of the complex anion is a metal to which hydroxyl ions are bound as ligands. The number of these ions depends on the normal coordination number of the metal. The cation of a hydroxo salt is usually an alkali metal, particularly sodium, or the alkaline earth metals barium, strontium and, in some cases, calcium. Heavy-metal salts can be prepared from a few hydroxo anions via a double decomposition reaction.

Hydroxo salts correspond closely to the well-known halo salts in their formula type and structure. Accordingly, mixed halo-hydroxo salts of a number of metals can be prepared. At elevated temperature, hydroxo salts can be converted into oxo salts, provided it is feasible to prepare the latter from a metal hydroxide (the central atom) and an alkali or alkaline earth metal hydroxide. In numerous systems, however, such oxometalates can be obtained only from oxides. In some cases, oxohydroxo salts are also formed as intermediates.

Complex hydroxometal anions are formed in solution via the following equilibrium reaction:

$$[M(OH)_x \rightleftarrows M^{x(+)} + x\,OH^-]$$

$$M^{x(+)} + y\,OH^- \rightleftarrows [M(OH)_y]^{(y-x)(-)}$$

The reagents are strong bases and poorly soluble metal hydroxides. In the above equations, the metal hydroxides function as "acids", in agreement with the modern theory of their amphoteric behavior. As far as is presently known, the following metals (arranged in order of increasing valence) form hydroxo salts:

M(II):	Be, Mg, Sn, Pb, Mn, Fe, Co, Ni, Cu, Zn, Cd
M(III):	Al, Ga, In, Bi, Cr, Mn, Fe
M(IV):	Sn, Pb, Pt
M(V):	Sb

The equilibrium distribution is of controlling importance in the preparation of crystalline alkali hydroxometalates. Most hydroxo salts, alkali salts in particular, rapidly decompose into their components in the presence of H_2O or dilute alkali hydroxide. Only the hexahydroxo salts of Sn (IV), Pt (IV) and Sb (V) dissolve in H_2O at room temperature without decomposition, whereas the other alkali hydroxometalates are stable only when they constitute the solid phase in the presence of (usually very concentrated) alkali hydroxide solution. The alkaline earth hydroxometalates are relatively sparingly soluble and hence are stable in dilute hydroxide; the compound $Ca[Zn(OH)_3]_2 \cdot 2\,H_2O$ is stable even in water. The equilibrium shifts toward the reagents with temperature.

Metal oxide–sodium oxide–water systems at constant temperature exhibit the same general behavior regardless of the particular compounds involved (see Fig. 341). Thus, with increasing alkali hydroxide concentration, the solubility at first increases to a maximum and then decreases sharply. The rising branch of the curve corresponds to solid $M(OH)_m$ or MO_n while the decreasing branch corresponds to sodium hydroxometalate, whose solubility is sharply reduced as the NaOH concentration increases.

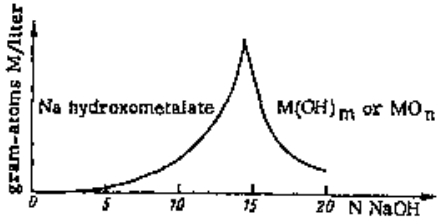

Fig. 341. Solubility of the system metal oxide-sodium oxide-water as a function of sodium hydroxide concentration.

The experimental fact that the sodium hydroxide concentration at the solubility maximum is usually over 30% indicates that highly concentrated (usually 45–50%) NaOH is required for the preparation of most alkali hydroxo salts. This is also necessary to ensure good yields. However, most alkaline earth hydroxometalates can be prepared from more dilute NaOH solutions.

Spreading the microcrystalline solid phase on a clay dish does not afford complete separation from the residual mother liquor. It has recently been established that alkali hydroxometalates can be separated from the mother liquor much more efficiently by brief shaking with pure isoamyl alcohol, and the alkaline earth salts by treatment with anhydrous methanol, possibly containing a small amount of NaOH.

Several types of hydroxo salts of some di- and trivalent metals can be prepared just as in the case of halo salts. These differ in the number of coordinated OH^- ions. The number of OH^- ligands depends on the concentration and temperature of the alkali hydroxide.

Among the less stable alkali hydroxometalates, it is often only the Na salt, but not the K salt, that can be prepared. This is due to the unusually high solubility of the corresponding K salts. In fact, the precipitation of the latter even from highly concentrated hydroxide solutions is often impossible without simultaneous crystallization of KOH. The rather sparingly soluble Ba and Sr salts can be precipitated from the metal hydroxide or oxide solutions by addition of Ba^{2+} or Sr^{2+}. The alkaline earth salts can be obtained more conveniently by simultaneous dropwise addition, in proper ratios, of concentrated solutions of the perchlorates of the central metal atom and of the alkaline earth metal to hot, moderately concentrated sodium hydroxide (sodium perchlorate is much more readily soluble in strong sodium hydroxide than is NaCl). The free hydroxo acids, which should exist as well-defined higher hydrates of the metal oxides, are not known, the exception being hexahydroxoplatinic (IV) acid, $H_2[Pt(OH)_6]$.

In some cases the fact that the hydroxometalates are chemical complexes is indicated by the color of the salts and of their solutions. The proof of structure is based on their thermal dehydration curve, their ability to form mixed halo-hydroxo salts, data on isomorphic relations, and some powder pattern studies.

DropBooks

Handling of Concentrated Alkali Hydroxides

STARTING MATERIALS

Very pure or reagent grade (97–98%) NaOH pellets and a similar grade of potassium hydroxide (containing an average of 85% of KOH, the remainder being H_2O) are used.

CONTAINER MATERIALS

Chemical glassware is sufficiently resistant to concentrated alkali hydroxide solutions at room temperature that it can be used without adversely affecting the purity of the products. However, hot, concentrated alkali hydroxide solutions attack any glass so strongly that the latter can be used at high temperatures only for short periods of time, if at all. Such experiments must therefore be run in refined silver containers, which resist even concentrated boiling alkali hydroxide solutions. While pure nickel containers are also suitable, they are not cheaper than silver.

FILTERS

Fritted Pyrex glass of medium and high porosity is suitable. However, its life may be limited in repeated use for filtering hot alkali hydroxide solutions. When filtering very hot and concentrated alkali hydroxide solutions, the glass suction funnel should be wrapped with a strong cloth so as to reduce as much as possible the ever-present danger of sudden breakage (this danger is real even with infrequently used filters). To prevent solidification of solutions containing more than 50% NaOH during filtration, the glass suction funnel is surrounded with a sheet metal jacket containing hot glycerol. When such solutions are boiled in a flask, the rubber stopper must be protected with an asbestos liner.

Even though filter plates made of certain plastics resist hot concentrated alkali hydroxide solutions, we have not yet tested them sufficiently to recommend them for laboratory use.

CARBONATE-FREE SODIUM HYDROXIDE

A 50% sodium hydroxide solution is prepared from the calculated amount of commercial NaOH in a silver flask. To prevent the occasional nuisance of the NaOH sticking to the bottom, the flask is vigorously shaken; solution is promoted by the strong, spontaneous heat evolution. However, external heating should be avoided because of the danger that the hot caustic solution will bump and spill out of the flask, a danger not obviated by the presence of a reflux condenser on the flask. The 50% hydroxide solution is allowed to cool slowly and, if possible, to stand at room temperature for 2-3 days. The precipitated Na_2CO_3 is then filtered off on glass frit of small pore size (rigorous exclusion of air). The completely clear filtrate is virtually carbonate-free. To avoid waiting for precipitation of the carbonate, one can add 1-2 g. of $Ba(OH)_2$ per 100 ml. of hot, 50% sodium hydroxide; the mixture may then be filtered immediately after cooling to room temperature.

Sodium hydroxide solutions of lower concentration can be prepared by dilution of the 50% solution with boiled H_2O. Removal of Na_2CO_3 from a solution containing more than 50% NaOH must be carried out at 40-60°C to prevent crystallization of NaOH. Such solutions may also be prepared by distilling the calculated amount of water from carbonate-free 50% sodium hydroxide into a graduated cylinder. For obvious reasons, CO_2 must be rigorously excluded. All equipment, including the reflux condenser and the glass suction filter, is protected with Peligot tubes (containing 50% KOH) held in place by rubber stoppers.

Handling alkali hydroxide solutions is often facilitated by a knowledge of their boiling points. For this reason, the boiling points of 20–70% NaOH and KOH solutions, taken from Gerlach [2], are tabulated below.

	25	42.8	53.8	66.7	81.8	100	122.2	150	233.3	g. NaOH (KOH)/ 100 g. H_2O
	20	30	35	40	45	50	55	60	70	% NaOH (KOH)
NaOH	108	116	121.5	128	134.5	142.5	150.5	160	180.5	B.p., °C
KOH	106	113	118	124.5	133	145	160.5	177.5	228	B.p., °C

SAFETY RULES

The destructive action of caustic alkali solutions begins immediately. Therefore, the eyes must always be protected by goggles which fit tightly on all sides. Any caustic solution under the fingernails should immediately be washed off with a large amount of water followed by dilute acetic acid. Silver being a much better heat conductor than glass, one should remember that silver equipment will get hot much more rapidly than glass.

DropBooks

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2. G. T. Gerlach. Z. anal. Chem. 26, 463 (1887); see also A. von Antropoff and W. Sommer. Z. phys. Chem. 123, 192 (1926).

Sodium Hydroxozincates

The system ZnO–Na_2O–H_2O contains the following four solid hydroxozincates, whose existence depends on the NaOH concentration:

$Na[Zn(OH)_3] \cdot 3\ H_2O$; $Na[Zn(OH)_3]$; $Na_2[Zn(OH)_4] \cdot 2\ H_2O$; $Na_2[Zn(OH)_4]$.

SODIUM TRIHYDROXOZINCATE, $Na[Zn(OH)_3]$

$$\underset{81.4}{ZnO} + \underset{40.0}{NaOH} + \underset{18.0}{H_2O} = \underset{139.4}{Na[Zn(OH)_3]}$$

PREPARATION OF CRUDE MATERIAL

A hot solution of 185 g. of NaOH in 100 ml. of H_2O is prepared, and ZnO (105 g.) is added. The mixture is refluxed 0.5 hours and cooled to 100°C. Water (85 ml.) is then gradually added through the condenser (use a funnel). The solution is filtered hot to remove residual ZnO and the filtrate is immediately cooled to about 15°C. If crystallization does not set in within a day, some NaOH pellets are dissolved in a few milliliters of the boiling zincate solution, the solution is cooled in a freezing mixture, and the resulting tetrahydroxozincate, which precipitates readily at this higher NaOH concentration, is used to seed an additional 5-ml. portion of the original zincate solution (moderate cooling). Rubbing with a glass rod initiates crystallization of the trihydroxozincate. The entire zincate solution is then seeded with this material. The precipitate obtained is filtered off after a few hours, washed with 50% sodium hydroxide, and dried on a clay plate in an empty desiccator. Yield: 50-60 g.

B. PREPARATION OF THE PURE COMPOUND

A solution (prepared at the boil) of 60 g. of ZnO and 250 ml. of pure, 51% sodium hydroxide is filtered at about 40°C, cooled to 15°C, and seeded with zincate prepared as described under (A). After 12 hours the mixture is filtered and worked up as under (A). Yield 40 g.

The moist product (10 g.) is shaken for two hours with 150 ml. of alkaline methanol solution (100 ml. of CH_3OH plus 15 g. of NaOH), filtered, washed first with the same methanol solution and then repeatedly with acetone, and dried over silica gel. This method removes the last traces of NaOH, and the analysis shows the calculated percentages of ZnO, Na_2O and H_2O.

PROPERTIES:

Colorless, microcrystalline powder (small rods). Decomposes immediately in water; decomposes after a few hours in 10% methanolic NaOH; stable in 15% methanolic NaOH (18°C). When prepared by method (A), contains about 0.1 moles of NaOH per mole of zincate.

SODIUM TETRAHYDROXOZINCATE, $Na_2[Zn(OH)_4]$

A carbonate-free, clear solution of 195 g. of NaOH in 140 ml. of H_2O is prepared, and ZnO (56 g.) is dissolved in it at the boil; the mixture is filtered at 90°C. The crystals that separate out after a few hours are washed with 50% NaOH and spread in as thin a

layer as possible on a clay dish. They are dried in an empty desiccator. Yield: about 100 g.

PROPERTIES:

Formula weight 179.42. Microcrystalline, thin platelets. The NaOH traces (about 0.2 moles per mole of zincate) cannot be removed.

REFERENCES:

R. Scholder and H. Weber. Z. anorg. allg. Chem. 215, 355 (1933); R. Scholder and G. Hendrich. Ibid. 241, 76 (1939); R. Scholder and K. Osterloh. Unpublished data.

Sodium Tetrahydroxomagnesate

$$Na_2[Mg(OH)_4]$$

$$\underset{58.3}{Mg(OH)_2} + 2\,\underset{80.0}{NaOH} = \underset{138.3}{Na_2[Mg(OH)_4]}$$

DropBooks

An approximately 65% NaOH solution is prepared in a silver flask by distilling 180 ml. of H_2O from 500 ml. of 50% sodium hydroxide. The solution is cooled to about 100°C and 6 g. of $Mg(OH)_2$, prepared by slaking MgO (calcined at 500°C) with hot H_2O, is added to it. The mixture is agitated with a silver stirrer and refluxed for 20 hours at 100°C in the absence of CO_2. Without interrupting the heating, the flask contents are transferred by suction (use silver tubing interconnected with polyethylene sleeves) onto a glycerol-heated, medium-pore-size fritted-glass filter, which is maintained at 100°C. The filter cake is dried by suction and immediately spread on a clay dish heated to 100°C. The dish is then kept for about five hours in a vacuum desiccator heated to 100°C, to promote absorption of the surface sodium hydroxide by the clay plate. This procedure yields 8–10 g. of relatively dry sodium hydroxomagnesate which is strongly contaminated with NaOH. To remove the NaOH, 3 g. of the crude product is pulverized in the absence of CO_2 and H_2O, and then shaken for 30–45 min. with freshly distilled isoamyl alcohol (b.p. 127–129°C). The mixture is suction-filtered (again in the absence of CO_2) through a medium-pore-size fritted-glass filter, and rinsed with 50 ml. each of isoamyl alcohol and ether. The product is then dried for a few hours over silica gel while simultaneously removing the ether in vacuum.

PROPERTIES:

Microcrystalline hexagonal platelets. Yields crystalline $Mg(OH)_2$ (brucite) on treatment with H_2O. Decomposed by strongly alkaline methanol or ethanol even below 0°C; isoamyl alcohol gradually splits off NaOH, but only on prolonged reaction.

REFERENCE:

R. Scholder and C. Keller. Unpublished data.

Sodium Tetrahydroxocuprate (II)

$$Na_2[Cu(OH)_4]$$

$$\underset{79.5}{CuO} + \underset{18.0}{H_2O} + 2\,\underset{80.0}{NaOH} = \underset{177.6}{Na_2[Cu(OH)_4]}$$

A. CRUDE MATERIAL

Very pure CuO (15 g.) is dissolved in a clear, carbonate-free solution of 500 g. of NaOH in 330 ml. of H_2O (brief refluxing). The dark-blue solution is cooled to 110°C and carefully diluted by adding 140 ml. of H_2O through the reflux condenser (use a funnel). The small quantity of unreacted CuO is then filtered off, collecting the filtrate in a preheated Erlenmeyer flask of refined silver. The Erlenmeyer flask is protected by a Peligot tube (filled with 50% KOH) and kept in an electric drying oven for six days at 75°C to allow the filtrate to crystallize. The mixture is then filtered; the crystals are washed with some 50% and 45% sodium hydroxide (once each) at room temperature and dried on a clay plate over H_2SO_4. Yield: 13 g.

B. PURIFICATION

The considerable amount of NaOH still present in the product is removed immediately following the washing with the 50% NaOH. Thus the dark-blue crystals are shaken for one hour with 150 ml. of 40% NaOH at room temperature and filtered.

The crystals are then shaken for one minute with the following solutions (in the order given): 150 ml. CH_3OH + 22.5 g. NaOH (18°C); 150 ml. CH_3OH + 15 g. NaOH (0°C); 150 ml. CH_3OH + 1.5 g. NaOH (−10°C).

After decantation, the solid is finally digested twice with pure methanol (−10°C), filtered and washed with methanol at −15°C. The crystals are placed on a clay plate and dried over silica gel in a minimum size desiccator.

When the cuprate solution remaining after filtering off the CuO is quickly cooled to room temperature in a freezing mixture, the salt precipitates as very thin, light-blue platelets. These, however, cannot be completely freed of the excess NaOH. Yield: 20 g.

PROPERTIES:

Firm, dark-blue crystals. The very pure salt obtained by method (B) is extremely sensitive to moisture and rapidly turns dark brown on exposure to air.

REFERENCES:

R. Scholder, R. Felsenstein and A. Apel. Z. anorg. allg. Chem. 216, 138 (1934); R. Scholder and K. Osterloh. Unpublished data.

Barium Hexahydroxocuprate (II)

$$Ba_2[Cu(OH)_6]$$

$$\underset{177.6}{Na_2[Cu(OH)_4]} + 2\,\underset{342.8}{Ba(OH)_2} = \underset{440.3}{Ba_2[Cu(OH)_6]} + 2\,\underset{80.0}{NaOH}$$

DropBooks

A solution of 10 g. of $CuBr_2$ in 25 ml. of H_2O is added to 200 ml. of carbonate-free 50% sodium hydroxide at +5°C. The resulting mixture is heated to 70°C (water bath) and the small amount of CuO filtered off. The filtrate is refluxed 130°C and a hot solution of 30 g. of $Ba(OH)_2 \cdot 8\ H_2O$ in 50 ml. of H_2O is added to it through a fluted filter (shaking). The salt that separates is immediately filtered off, cooled to 0°C in an Erlenmeyer flask, shaken for 5 min. with 100 ml. of methanol at −10°C, and filtered off. It is washed with methanol at 0°C and then thoroughly with acetone and anhydrous ether. The residual ether is removed by prolonged vacuum treatment in a desiccator. The product is completely pure. Yield: 13 g.

PROPERTIES:

Light-blue powder (rhombic crystal aggregates). Decomposed by H_2O.

REFERENCES:

R. Scholder, R. Felsenstein and A. Apel. Z. anorg. allg. Chem. 216, 138 (1934); R. Scholder and V. Voelskow. Unpublished data.

Sodium Tetrahydroxoferrate (II)

$Na_2[Fe(OH)_4]$

$$\underset{55.9}{Fe} + 2\,\underset{80.0}{NaOH} + 2\,\underset{36.0}{H_2O} = \underset{169.9}{Na_2[Fe(OH)_4]} + H_2$$

The reactor is a round-bottom, refined-silver flask, carrying a rubber stopper holding a reflux condenser protected by a Peligot tube (filled with an alkaline pyrogallol solution) and a silver tube serving as inlet for pure nitrogen. The flask is charged with 8 g. of reduced iron and 350 ml. of a 50% solution of pure NaOH. The air is displaced with N_2 and the mixture is refluxed for 2.5 hours in a steady N_2 stream. The blue solution is cooled to 120°C and suction-filtered (in the absence of air) through a glass frit covered with a layer of reduced iron. The filtrate is collected in a Pyrex suction flask containing 100 ml. of 50% sodium hydroxide, through which a nitrogen stream may be passed. The filtrate is allowed to cool for about 12 hours under N_2; the gray-green precipitate is then filtered off under N_2, washed with 50% sodium hydroxide, and dried on a clay dish in a nitrogen-filled desiccator. Yield: 4 g.

PROPERTIES:

Gray-green microcrystalline powder (polyhedral crystals); very sensitive to moisture and O_2. Besides the polyhedra, microscopic examination also reveals colorless platelets with oblique sides of $Na_4[Fe(OH)_7] \cdot 2\,H_2O$ (see p. 1689).

REFERENCE:

R. Scholder, Angew. Chem. 49, 255 (1936).

Strontium Hexahydroxonickelate (II)

$Sr_2[Ni(OH)_6]$

$$\underset{257.6}{Ni(ClO_4)_2} + 2\,\underset{573.1}{Sr(ClO_4)_2} + 6\,\underset{240.0}{NaOH} = \underset{336.0}{Sr_2[Ni(OH)_6]} + 6\,\underset{794.7}{NaClO_4}$$

A mixture of 250 g. of NaOH and about 8 g. of $Sr(OH)_2 \cdot 8\,H_2O$ is dissolved in 455 ml. of H_2O contained in a silver flask. The solution is briefly refluxed and allowed to stand for 24 hours; the $SrCO_3$ precipitate is then filtered off. The solution is then brought to a boil, and 35 ml. of a $Ni(ClO_4)_2 : Sr(ClO_4)_2$ solution (molar ratio ~ 1:4) is added. The latter solution is prepared by adding

25 ml. of H_2O to 6.5 g. of $NiCl_2 \cdot 6\,H_2O$ and 16 g. of $SrCO_3$, then gradually adding 25 ml. of 70% $HClO_4$. To remove HCl, the solution is concentrated until dense $HClO_4$ fumes are evolved, and then diluted with H_2O to 35 ml. After addition of the perchlorate solution, the reactor mixture is refluxed in the absence of CO_2. The $Sr_2[Ni(OH)_6]$ precipitate is filtered off with suction while the mother liquor is still hot (use small-pore-size glass frit), with thorough exclusion of CO_2; it is washed with 35% NaOH at room temperature, and then with absolute methanol. The precipitate is shaken for eight hours with absolute methanol, filtered, and washed with methanol and ether. The product is dried and freed of ether by keeping it for several hours in vacuum in a desiccator containing silica gel.

PROPERTIES:

Gray-green, very fine crystalline powder of unidentifiable crystalline habit; not attacked by half-saturated aqueous $Sr(OH)_2$ solution (0.35 g. SrO/100 ml. H_2O); gradually decomposed by H_2O.

REFERENCE:

R. Scholder and E. Giesler, Unpublished data.

DropBooks

Sodium Trihydroxostannate (II)

$Na[Sn(OH)_3]$

$$\underset{189.6}{SnCl_2} + 2\,\underset{80.0}{NaOH} = \underset{152.7}{Sn(OH)_2} + 2\,\underset{116.9}{NaCl}$$

$$\underset{152.7}{Sn(OH)_2} + \underset{40.0}{NaOH} = \underset{192.7}{Na[Sn(OH)_3]}$$

Tin (II) hydroxide is prepared by treating a milky solution of 25 g. of $SnCl_2 \cdot 2\,H_2O$ in 1.5 liters of H_2O with a small excess of approximately 10% ammonia (room temperature), diluting to two liters, allowing the solid to settle, removing the slightly turbid supernatant by aspiration, adding two liters of H_2O, again removing the supernatant, and then repeating this process 2–3 times. The precipitated $Sn(OH)_2$ is filtered off on a large Pyrex glass frit of medium pore size, at first without suction, then by slowly applying vacuum; it is then washed until essentially chloride-free. The product is thoroughly dried by suction, calcined to SnO_2, and analyzed for $Sn(OH)_2$ content. Yield of $Sn(OH)_2$: 85%; $Sn(OH)_2$ content: about 50%.

Reagent grade NaOH (35 g.) is dissolved in 23 ml. of water contained in a wide-mouth 150-ml. Erlenmeyer glass flask

solution is cooled to 50–60 °C and the entire $Sn(OH)_2$ paste is added to it, even though some crystalline NaOH may be present. The container is immediately closed off with a rubber stopper carrying a Peligot tube filled with an alkaline pyrogallol solution. The $Sn(OH)_2$ after brief shaking dissolves while a small amount of dark SnO separates from the sodium hydroxide solution (the concentration of which is now 50%). The mixture is filtered warm through small-pore-size glass frit. The clear filtrate is protected from air and kept at 0 °C; after a few hours, crystallization of the salt is complete. The mixture is carefully warmed to 8 °C and filtered through large-pore-size glass frit. To remove the mother liquor still on the crystals, the latter are spread on a clay dish precooled to 0 °C, and the dish is kept for 12 hours at 0–3 °C in an evacuated desiccator. Yield: 6 g.

PROPERTIES:

Colorless, partly clustered small rods, pointed at the ends. When stored for some time in a closed container (even at 0 °C) turns dark because of decomposition; very sensitive to moisture and O_2. After removal from the clay dish, the product is still contaminated with 0.1–0.2 moles of NaOH per mole. During separation and drying, a small percentage of the Sn (II) is converted to Sn (IV).

REFERENCES:

R. Scholder and R. Pätsch, Z. anorg. allg. Chem. 216, 176 (1933); R. Scholder and K. Krauss, Unpublished data.

Sodium Hexahydroxochromate (III)

$$Na_3[Cr(OH)_6]$$

$$\underset{350.4}{Cr(ClO_4)_3} + \underset{240.0}{6\,NaOH} = \underset{223.1}{Na_3[Cr(OH)_6]} + \underset{367.4}{3\,NaClO_4}$$

Since commercial chromic hydroxide always contains an appreciable percentage of carbonate, sodium hexahydroxochromate (III) is best prepared from an aqueous $Cr(ClO_4)_3$ solution obtained from Cr_2O_3 · aq.; the $NaClO_4$ formed by reaction with NaOH is sufficiently soluble even in highly concentrated NaOH.

A sample of commercial Cr_2O_3 · aq. of known Cr_2O_3 content corresponding to 3 g. of Cr_2O_3 is dissolved in the stoichiometric quantity of 20–25% $HClO_4$. The solution is concentrated to 25 ml. and filtered; the filtrate is then added to 300 ml. of carbonate-free 50% NaOH. The mixture is refluxed for about 0.5 hours, cooled to

about 120°C, and filtered into a suction flask preheated to 85°C. The dark-green filtrate is transferred to a silver flask protected by a Peligot tube (filled with 50% KOH) and allowed to stand for about four hours in an electric drying oven at 85°C. The precipitated hexahydroxochromate is washed twice with some 40% NaOH (18°C), shaken for 0.5 hours with 80 ml. of 5% methanolic NaOH (18°C), washed several times with the same alkaline methanol solution, and, finally, thoroughly washed with acetone; the acetone is then removed by prolonged vacuum evaporation in a desiccator containing silica gel. The product is very pure (Cr : Na = 1 : 2.99–3.02). Yield: 5–6 g.

On cooling, the $Na_3[Cr(OH)_6]$ mother liquor deposits tightly clustered platelets of mixed crystals of hepta- and octahydroxochromate (III).

PROPERTIES:

Microcrystalline green powder (well-formed polyhedra). At first soluble in cold H_2O, affording a clear solution, which after a long time gradually yields a flocculent precipitate of $Cr_2O_3 \cdot aq$.

REFERENCE:

R. Scholder and R. Pätsch. Z. anorg. allg. Chem. 220, 411 (1934).

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Sodium Hydroxoferrates (III)

These products are obtained by the oxidation of a solution of $Na_3[Fe(OH)_4]$ in 50% NaOH with O_2. Under otherwise identical conditions, sodium octahydroxoferrate (III) is formed at 20–25°C, heptahydroxoferrate (III) at 50–60°C, and olive-green oxoferrate (III) at 100–130°C. Boiling 55–60% NaOH yields the red oxoferrate (III), $NaFeO_2$.

SODIUM HEPTAHYDROXOFERRATE (III), $Na_4[Fe(OH)_7] \cdot 2\,H_2O$

I. $$2\,Na_3[Fe(OH)_4] + 4\,NaOH + \tfrac{1}{2}O_2 + H_2O = 2\,Na_4[Fe(OH)_7](2\,H_2O)$$

339.8 160.0 16.0 605.9

A solution of $Na_3[Fe(OH)_4]$ in 50% NaOH, prepared as described on p. 1686 and cooled to 120°C, is filtered into an Erlenmeyer flask containing 100 ml. of 50% NaOH. This flask is connected to two wash bottles each containing 50% KOH, and a fast O_2 stream is passed through the solution (kept at 60°C) for about 2 hours. This causes a gradual discoloration of the greenish-blue solution

and simultaneous crystallization. The crystals are filtered off, rapidly washed with 50% NaOH, and dried as a thin layer on a clay dish in an empty desiccator containing silica gel.

The oxidation with Br_2 is more elegant. The flask containing $Na_2[Fe(OH)_4]$ solution is closed off with a rubber stopper carrying a Peligot tube and a dropping funnel. Then a solution of 2–3 ml. of Br_2 in 10 ml. of CCl_4 is added dropwise at 50–60°C with vigorous agitation until the iron solution just turns colorless. An excess of Br_2 must be avoided. The mixture is allowed to stand for two hours at the same temperature and filtered.

II. Freshly precipitated, thoroughly washed $Fe_2O_3 \cdot aq.$ is added to carbonate-free 50% NaOH. An amount of NaOH equal in weight to the water contained in the Fe_2O_3 paste is then added and the latter is dissolved with moderate heating (not to exceed 60°C). The mixture, in a silver Erlenmeyer flask protected with a Peligot tube (filled with 50% KOH), is allowed to stand for several days in an electric drying oven at 70°C. In this manner, the $Fe_2O_3 \cdot aq.$ is completely converted into the nearly colorless, microcrystalline $Na_4[Fe(OH)_7] \cdot 2\ H_2O$, which is sparingly soluble in concentrated NaOH.

PROPERTIES:

Nearly colorless crystalline powder (beveled, partly clustered platelets); very sensitive to moisture. Instantly decomposed by H_2O and CH_3OH, affording $Fe_2O_3 \cdot aq.$ Unstable even in 30% NaOH (18°C).

SODIUM OCTAHYDROXOFERRATE (III), $Na_5[Fe(OH)_8] \cdot 5\ H_2O$

Oxidation of $Na_2[Fe(OH)_4]$ with O_2 in a strongly alkaline solution (see method I above) at 20°C yields fine needles of octahydroxoferrate (III), which is also nearly colorless. When allowed to stand at room temperature for a few days, freshly prepared $Fe_2O_3 \cdot aq.$ (see method II above) is converted to a large extent, but never completely, to the same salt.

REFERENCES:

R. Scholder, Angew. Chem. 49, 255 (1936); R. Scholder and K. Krause, Unpublished data.

Barium Hydroxoferrates (III)

Barium hydroxoferrates (III) are prepared by dropwise addition of an $Fe(ClO_4)_3$-$Ba(ClO_4)_2$ solution to hot NaOH. If the initial

NaOH concentration is 25–39%, a precipitate of the hexahydroxo salt, $Ba_3[Fe(OH)_6]_2$, is obtained; however, if this NaOH concentration exceeds 42%, the heptahydroxo salt, $Ba_2[Fe(OH)_7] \cdot {}^1/_2\ H_2O$, precipitates.

The starting $Fe(ClO_4)_3$–$Ba(ClO_4)_2$ solution (1:3 molar ratio) is obtained by dissolving 3.5 g. of Fe_2O_3 (analytical grade) in a mixture of 35 ml. of 70% $HClO_4$ and 25 ml. of conc. HCl. To eliminate the HCl, the solution is concentrated until dense fumes of $HClO_4$ are given off. The resulting solution is added, with agitation, to a slurry of 26 g. of $BaCO_3$ in 125 ml. of H_2O; the mixture is then filtered.

BARIUM HEXAHYDROXOFERRATE (III), $Ba_3[Fe(OH)_6]_2$

The starting 33% NaOH is prepared by diluting 180 ml. of carbonate-free 50% NaOH with 140 ml. of CO_2-free H_2O in a refined silver flask. The mixture is heated to reflux with exclusion of CO_2, and 75 ml. of the above $Fe(ClO_4)_3$–$Ba(ClO_4)_2$ solution is added dropwise. A white precipitate of $Ba_3[Fe(OH)_6]_2$ forms immediately. The mixture is allowed to reflux for one hour, after which it is cooled to room temperature, suction-filtered through a medium-pore-size glass frit, and washed with a small amount of 33% NaOH. The precipitate is vigorously shaken for a few minutes with 200 ml. of absolute methanol, filtered through a small-pore-size glass frit, and washed with absolute methanol and anhydrous ether. It is then dried for one hour in a vacuum desiccator over silica gel.

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PROPERTIES:

White to slightly yellowish hexagonal platelets. Decomposed by H_2O, affording $Fe_2O_3 \cdot aq.$; stable in absolute methanol.

BARIUM HEPTAHYDROXOFERRATE (III), $Ba_2[Fe(OH)_7] \cdot {}^1/_2\ H_2O$

The preparation of this compound is analogous to that of $Ba_3[Fe(OH)_6]_2$. However, instead of 33% sodium hydroxide, 400 ml. of 50% NaOH is used.

PROPERTIES:

White to slightly yellowish hexagonal platelets. Decomposed by H_2O, affording $Fe_2O_3 \cdot aq$. Prolonged contact with absolute methanol yields a brown solution.

Strontium hexahydroxoferrate (III), $Sr_3[Fe(OH)_6]_2$, can be prepared in a similar way, using 5% NaOH, while strontium heptahydroxoferrate (III), $Sr_2[Fe(OH)_7] \cdot 3\ H_2O$, requires 20% NaOH.

REFERENCE:

R. Scholder, W. Zeiss and M. Kreutz. Unpublished data.

Alkali Aluminates

Depending on the temperature, the following three sodium aluminates crystallize from a solution containing NaOH and Al_2O_3 in equal concentrations:

tetrasodium heptahydroxoaluminate $Na_4[Al(OH)_7] \cdot 3\ H_2O$
monosodium oxohydroxoaluminate I $Na_2O \cdot Al_2O_3 \cdot 2.67\ H_2O = Na_8[Al_8O_4(OH)_{18}]$
monosodium oxohydroxoaluminate II $Na_2O \cdot Al_2O_3 \cdot 2.5\ H_2O = Na_4[Al_4O_3(OH)_{10}]$

Only monopotassium oxohydroxoaluminate, $K_2O \cdot Al_2O_3 \cdot 3\ H_2O = K_2[Al_2O(OH)_8]$, is obtained from a potassium aluminate solution.

TETRASODIUM HEPTAHYDROXOALUMINATE, $Na_4[Al(OH)_7] \cdot 3\ H_2O$

$$\underset{78.0}{Al(OH)_3} + \underset{160.0}{4\,NaOH} = \underset{(\cdot 3\ H_2O)\ 292.1}{Na_4[Al(OH)_7]}$$

Aluminum hydroxide (45 g.) is dissolved in a solution of 130 g. of NaOH in 100 ml. of H_2O by refluxing one half hour. The solution is slowly cooled to room temperature, allowed to stand for six hours, and only then filtered through a small-pore-size glass frit to remove the considerable amount of Na_2CO_3 precipitate [commercial $Al(OH)_3$ often contains a large percentage of carbonate]. The crystallization of sodium aluminate, which usually takes a long time to develop, does not start during this period. The clear filtrate is transferred to a round-bottom glass flask closed off with rubber stoppers carrying an air-tight agitator and a Peligot tube. The flask is immersed in 18 °C water and its contents are vigorously stirred for 10–14 hours. A thick crystal slurry is formed; this is dried by suction, spread out in a thin layer on a clay dish, and finally dried in an empty desiccator. Yield: 38 g.

PROPERTIES:

Microcrystalline powder; strongly birefringent oblong prisms with beveled end faces. Soluble in H_2O. Contains (as impurity) 0.2–0.3 moles of NaOH per mole of aluminate.

MONOSODIUM OXOHYDROXOALUMINATE I, $Na_6[Al_6O_4(OH)_{16}]$

A clear aluminate solution is prepared in the manner described above and stirred for 8–10 hours at 40–45 °C. The crystal slurry is washed with 50% NaOH, covered with methanol, and shaken for 0.5 hours with 150 ml. of methanol. The mixture is filtered, thoroughly washed with a large quantity of methanol followed by acetone, and vacuum-dried over silica gel. Yield: 24 g. Analysis shows Al : Na = 1 : 1.02–1.04.

PROPERTIES:

Formula weight 636.15. Microcrystalline powder (square plates with beveled edges). Transient solubility in H_2O.

MONOSODIUM OXOHYDROXOALUMINATE II, $Na_4[Al_4O_3(OH)_{10}]$

The aluminate solution (see above) is stirred for about six hours at 100–105 °C. Otherwise, the preparation, isolation, purification and drying are the same as described above. Very pure product is obtained.

PROPERTIES:

Formula weight 417.98. Microcrystalline powder (thin polygonal platelets).

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MONOPOTASSIUM OXOHYDROXOALUMINATE, $K_2[Al_2O(OH)_6]$

A solution prepared at the boil from 120 g. of KOH, 30 g. of $Al(OH)_3$, and 100 ml. of H_2O is allowed to stand for several hours at room temperature, filtered, seeded with the salt (see below), and shaken for 24 hours. The microcrystalline solid deposit is washed with a small amount of 50% KOH, then with 150 ml. of methanol containing 5% KOH, and finally with acetone; it is then vacuum-dried over silica gel. Yield: 5 g.

Without seeding, the crystallization is delayed for several days. The seeding crystals are obtained by preparing a solution containing 20 g. of KOH, 5 g. of $Al(OH)_3$, and 10 ml. of H_2O, filtering at room temperature, and shaking for 12 hours. This produces an abundant crop (about 6.5 g.) of monopotassium aluminate crystals. These crystals, however, are very small and are difficult to free from the adhering KOH, particularly if the latter is very concentrated.

PROPERTIES:

Formula weight 250.20. Microcrystalline powder (polyhedra); incompletely soluble in water. Can be obtained very pure.

REFERENCES:

R. Fricke and P. Jucaitis. Z. anorg. allg. Chem. 191, 129 (1930); R. Scholder, W. Kleeberg and M. Schröder. Naturforschung und Medizin in Deutschland, 1939-1946 (FIAT Review), Vol. 25, Inorg. Chem., part III, p. 141.

Sodium Hexahydroxostannate (IV)

$Na_2[Sn(OH)_6]$

$$\underset{188.7}{Sn(OH)_4} + 2\,\underset{80.0}{NaOH} = \underset{266.8}{Na_2[Sn(OH)_6]}$$

A solution of $SnCl_4$ in very dilute hydrochloric acid is neutralized to methyl orange with carbonate-free NaOH. The SnO_2 · aq. precipitate is filtered off, washed until chloride-free with H_2O, and added in portions to an excess of concentrated, 100 °C NaOH, in which it dissolves rapidly, affording a clear solution. The crystalline hexahydroxostannate precipitates after a short time. The crystal slurry is filtered in the absence of CO_2 and washed with 30% NaOH and then several times with ethanol and ether.

PROPERTIES:

Colorless crystalline powder (thin hexagonal leaflets). Readily soluble in H_2O; the solubility decreases markedly with temperature (see Reiff and Toussaint). Always contains small amounts of adsorbed NaOH. Very sensitive to CO_2.

REFERENCES:

H. Zocher. Z. anorg. allg. Chem. 112, 1 (1920); R. Reiff and S. M. Toussaint. Ibid. 241, 372 (1939).

Sodium Hexahydroxoplumbate (IV)

$Na_2[Pb(OH)_6]$

1. ELECTROCHEMICAL METHOD

$$\underset{281.2}{Na[Pb(OH)_3]} + \underset{40.0}{NaOH} + 2\,OH^- - 2\,e = \underset{355.3}{Na_2[Pb(OH)_6]}$$

Yellow PbO (analytical grade, 18.5 g.) is dissolved in 300 ml. of boiling 13N NaOH; the solution is suction-filtered through a

small-pore-size glass frit and allowed to cool in a CO_2-free atmosphere. This hydroxoplumbate (II) solution is unstable and on prolonged standing gradually deposits crystalline lead oxide. Hence it should be electrolyzed as soon as it has cooled to room temperature. Sometimes it may be necessary to separate the solution from the precipitated PbO by decantation right after cooling.

A rectangular 300-ml. glass jar covered with a rubber plate forming an air-tight seal is used as the electrolysis cell. Through appropriate openings in the lid the tank is provided with a gas outlet tube, a thermometer, an air-tight stirrer, an anode lead-in wire cemented into a glass tube, and a porous clay cell serving as the cathode space. The entire system must be gas-tight. Smooth platinum electrodes (5 × 5 cm.) are used. The electrolysis is carried out at ambient temperature with a current density of 0.12–0.18 amp./in.^{2}, while vigorously stirring the strongly alkaline hydroxoplumbate (II) solution in the anode space. The cathode space contains concentrated NaOH. The plumbate (IV) separates in the form of a white crystalline precipitate. The precipitate is allowed to settle, the clear solution is siphoned off, and the crystal slurry is covered with absolute ethanol. The crystals and liquid are then transferred to a smaller container and repeatedly digested with absolute ethanol until the latter no longer shows an alkaline reaction. The pure white crystals become slightly yellowish on vacuum drying in a desiccator.

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II. CHEMICAL METHOD

$$\underset{443.4}{Pb(CH_3COO)_4} + \underset{240.1}{6\,NaOH} = \underset{355.3}{Na_2[Pb(OH)_6]} + \underset{328.2}{4\,CH_3COONa}$$

A one-liter, round-bottom glass flask equipped with an air-tight stirrer, a dropping funnel and a Peligot tube (filled with 30% KOH), all inserted through rubber stoppers, is charged with 200 ml. of carbonate-free 30% NaOH. The tip of the dropping funnel is inserted into a short glass tube (15 mm. I.D.) to protect it from the splashing NaOH solution. A solution (usually yellowish) of 50 g. of $Pb(CH_3COO)_4$ in 200 ml. of K_2CO_3-dried chloroform containing 1 ml. of glacial acetic acid (filtered, if necessary) is added drop-by-drop with vigorous stirring. The brown PbO_2, formed at the site of contact between the drops of the chloroform solution and the NaOH in the flask, dissolves rapidly; after a while, $Na_2[Pb(OH)_6]$ begins to precipitate. Following the addition of the chloroform solution, the mixture is stirred until the crystalline suspension is pure white. The precipitate is allowed to settle for several hours; it is then filtered off and washed twice with 30% NaOH and at least five times with methanol containing 1%

alkali. During this procedure, atmospheric moisture and CO_2 must be absent. The precipitate is then dried on a clay dish placed in an evacuated desiccator over silica gel. A pure white product is obtained provided processing is rapid. Yield: 33 g.

Should the salt be yellowish, it can be purified as follows. The moist product is added in small portions to 500 ml. of 15% NaOH at 75°C (agitation), making sure that each portion is completely dissolved before adding the next. The small residue is filtered off, 150 g. NaOH is added to the filtrate while it is still hot, and the mixture is vigorously shaken to complete dissolution. After cooling, the pure white crystalline powder is filtered off and washed and dried as described above. Yield: 26 g.

PROPERTIES:

Colorless crystalline powder (hexagonal polyhedra); stable in 2% NaOH at 18°C; very sensitive to moisture. Discolors after absorbing H_2O. Always contains some excess NaOH.

REFERENCES:

I. G. Grube. Z. Electrochem. 28, 273 (1922); A. Simon. Z. anorg. allg. Chem. 177, 109 (1929).
II. R. Scholder. Unpublished data.

Barium Oxohydroxostannate (II)

$$Ba[Sn_2O(OH)_4]$$

$$\underset{385.5}{2\,Na[Sn(OH)_3]} + \underset{171.4}{Ba(OH)_2} = \underset{458.8}{Ba[Sn_2O(OH)_4]} + \underset{80.0}{2\,NaOH} + \underset{18.0}{H_2O}$$

The entire $Sn(OH)_2$ paste obtained from 25 g. of $SnCl_2 \cdot 2\,H_2O$ (preparation as for $Na[Sn(OH)_3]$, p. 1687) is added to a 50°C solution of 60 g. of NaOH in 50 ml. of H_2O. The mixture is cooled to 30°C and a hot solution of 1 g. of $Ba(OH)_2 \cdot 8\,H_2O$ in 2 ml. of H_2O is added. The mixture is allowed to stand at this temperature for about one hour (air must be absent) and is then filtered to remove the dark SnO and the precipitated carbonate. The clear filtrate is heated to 65°C and treated with a hot solution of 9 g. of $Ba(OH)_2 \cdot 8\,H_2O$ in 20 ml. of H_2O (95°C). The greenish-yellow barium oxohydroxostannate precipitates within a few minutes. The supernatant is decanted; the solid is filtered off and covered with 50% NaOH. The salt is then washed with 50 ml. of 2% $Ba(OH)_2 \cdot 8\,H_2O$ solution in methanol, followed by pure, 0°C methanol; it is dried on a clay dish over silica gel. Yield: 5 g. Slightly contaminated with $BaCO_3$.

PROPERTIES:

Yellowish microcrystalline powder (plates beveled at ends). Decomposed by H_2O.

REFERENCES:

R. Scholder and R. Pätsch. Z. anorg. allg. Chem. 216, 176 (1933); R. Scholder and K. Krauss. Unpublished data.

DropBooks

SECTION 3

Iso- and Heteropoly Acids and Their Salts

B. GRÜTTNER AND G. JANDER

Introduction

ISOPOLY COMPOUNDS

Compounds with higher aggregated anions, in which the anion-forming element occurs at least twice, are termed isopoly compounds. Usually it is the alkali or ammonium salts of the isopolyacids that are synthesized. Compounds with isopolyanions are formed, among others, by boron, silicon, phosphorus, arsenic, sulfur, vanadium, molybdenum and tungsten. They may be prepared in a number of ways, e.g., by fusion of an acid anhydride with an alkali hydroxide, dehydration of acid salts, or treatment of a normal salt with its acid anhydride.

Derivatives of the weaker, oxygen-containing metallic acids, such as those of tungstic, molybdic or vanadic acids, exhibit a quite characteristic behavior, and may therefore be considered as the "classical" isopoly compounds. One property characteristic of these metallic acids is the more or less sharply pronounced hydrolysis of their salts in aqueous solution, particularly in the presence of H^+ ions. The hydrolysis products then undergo, over a period of time, a secondary reaction, combining to more highly aggregated ions, that is, the isopolyanions. For example:

$$6\,(WO_4 \cdot aq.)^{2-} + 6\,H^+ \rightleftarrows 6\,(HWO_4 \cdot aq.)^-$$
$$6\,(HWO_4 \cdot aq.)^- + H^+ \rightleftarrows (HW_6O_{21} \cdot aq.)^{5-} + 3\,H_2O.$$

In addition, the following rules apply to the isopoly compounds of vanadium, molybdenum and tungsten.

Specific isopolyanions of definite degrees of condensation and specific chemical properties predominate in the solution; their existence is a function of the H^+ concentration and their crystalline salts may be isolated if certain conditions are observed. When solid, almost all salts of these isopolyacids contain water of crystallization. In keeping with their structure, these compounds

are very sensitive to OH^-, which rapidly degrades most of them to simple molecular compounds. The free acids cannot be isolated since the presence of excess H^+ causes progressive aggregation until insoluble high-molecular-weight hydrated oxides precipitate. "Metatungstic acid" (dodecatungstic acid) is an exception; its overall chemical and crystallographic behavior places it among the heteropoly compounds; thus, it will be discussed in that section.

The preparation of polyphosphates, polysilicates and polyborates is discussed in sections on the respective elements, e.g., on pages 546 ff., 697 ff., 793 ff., and 704 ff. of this handbook.

HETEROPOLY COMPOUNDS

Heteropoly compounds are composed not only of the weak, oxygen-containing metallic acids (tungstic, molybdic and vanadic), but also of moderately strong to weak acids of nonmetals, e.g., boric, silicic, phosphoric, arsenic, telluric, etc., acids. Stable heteropoly compounds very frequently show nonmetallic to metallic acid ratios of 1:12, 1:6 or 1:9. Since the heteropoly compounds form under conditions similar to those in which isopoly compounds are obtained, that is, only in solutions containing H^+ ions, it is assumed that the building blocks of the heteropolyanions are isopolyanions [1].

In keeping with their constitution, all compounds of this class are quite unstable in the presence of OH^- ions and are degraded to the simple metallic and nonmetallic acids. The careful degradation of very complex heteropolyanions by agents such as K_2CO_3, which act as weak sources of hydroxyl ions, permits the isolation of several intermediates, but nothing further is yet known concerning the mechanism. The heteropolyacids are somewhat more stable to H^+ ions, so that partial isolation of the free acids is possible. Further characteristic properties of numerous heteropoly compounds include their good crystallizability and their relatively high water content per mole of the solid. No heteropoly compounds lacking water in the anion complex are known. Another peculiarity of this class of compounds is that many of the free acids, as well as their salts, crystallize isomorphously [2]. The free acids are rather basic and the formation of neutral salts occurs only as an exception; generally, only acid salts can be isolated. The free acids are specifically capable of forming heavy, oily addition compounds with ether, even when the latter is in the vapor form; these have only a limited miscibility with water and excess ether and easily decompose [3]. This property is commonly used in the preparation of the crystalline acids (see below).

In general the heteropoly compounds of tungstic acid are more complexed and more resistant to hydrolysis than those of molybdic

or even vanadic acid. The stability within the same class of compounds varies depending on the nonmetallic acid, so that compounds with phosphoric and silicic acids are more stable than those containing arsenic acid.

Several recently described compounds of molybdic and tungstic acids with phosphoric acid, where the ratio of Mo (or W)/P is below 3:1 (e.g., 2 $MoO_3 \cdot P_2O_5$ or $Na_2O \cdot 2\ WO_3 \cdot P_2O_5$), are not heteropoly compounds; rather, the Mo or W is bound as a cation [4]. We shall omit their discussion.

REFERENCES:

1. G. Jander and K. F. Jahr. *Kolloid-Beihefte* 41, 297 (1935).
2. See, e.g., A. Rosenheim and J. Jaenicke. Z. anorg. Chem. 77, 239 (1912); 101, 235 (1917); H. Copaux. Ann. Chim. Phys. [8] 17, 207 (1909); R. Abegg. Handbuch d. anorg. Chem. [Handbook of Inorganic Chemistry], Vol. IV., part 1, 2nd half, p. 993.
3. E. Drechsel. Ber. dtsch. chem. Ges. 20, 1452 (1887); A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. 101, 224, 250 (1917).
4. I. Schulz. Ibid. 281, 99 (1955); 284, 31 (1956).

General Methods

1. FREE HETEROPOLYACIDS BY THE METHOD OF DRECHSEL

A solution of the sodium salt of a heteropoly acid is concentrated as far as possible (even to the sirupy state), placed in a separatory funnel, and covered with about 1/3 its volume of ether. The funnel is shaken vigorously to saturate the solution with the ether. Ice-cold, conc. (37%) iron-free HCl is now added in small portions, with vigorous shaking after each addition. The liquid must not be allowed to heat up during this step; if necessary, the separatory funnel should be externally cooled with water. The liberated acid immediately forms an adduct with the ether and sinks to the bottom as heavy, oily drops which form a third layer. When this layer clarifies, it is drained into a flask. The reaction is complete when addition of hydrochloric acid does not produce further oily droplets at the ether-solution interface. The oil is treated with about an equal volume of H_2O, and the ether is driven off by drawing a stream of clean, dry air through the mixture. The residual clear aqueous solution of the acid is placed, until incipient crystallization, in a vacuum desiccator over conc. H_2SO_4 and then over solid KOH to absorb the still present HCl. Only the 12-tungstic-1-boric acid should be crystallized in desiccator over P_2O_5, in which case this is done to

prevent decomposition of the heteropolyacid by volatilization of the boric acid. Only hydrochloric acid should be used for extraction since the ether adduct is always capable of absorbing this acid, and the latter can then be removed more readily than either sulfuric or nitric acids.

2. FREE HETEROPOLYACIDS VIA ION EXCHANGE

The advantage of this method lies in the high purity of the final product. The starting materials—heteropoly salts prepurified by many recrystallizations and extremely soluble in water—are best prepared by the method given below (see 3). In view of the very pronounced acidity of the heteropolyacids and their frequent sensitivity to reducing agents, it is desirable to use cation exchange resins carrying sulfonic acid groups (e.g., Permutit RS), which exhibit only a strong acid function and have almost no reducing power. The operating conditions depend on the sensitivity, quality and quantity of the heteropolyacid to be prepared, and can easily be optimized in preliminary experiments. The following rules of thumb should be observed: The exchange capacity of the resin normally amounts to about 2 meq./cm^3 (bulk volume); it is desirable to work with starting solutions which are as concentrated as possible; the throughput of the solution through the column should be low (approx. 2–5 cm^3/min.). The free heteropolyacid solutions should be concentrated on a steam bath or in a desiccator and, if needed, crystallized.

The method fails with heteropolysalts whose aqueous solutions exhibit a strong acid reaction. Additional complications arise if salt impurities (NaCl, $NaNO_3$, etc.) are present in the solution, since these salts produce HCl, HNO_3, etc., during passage through the column. A too strongly acid medium hinders the formation of free, crystalline heteropolyacids during concentration of the eluate.

The one advantage of this method has already been mentioned. The disadvantages are that one must begin with pure, crystalline alkali salts (which in some cases can only be obtained by the roundabout route of first preparing the free acid by Drechsel's method), and, in addition, the heteropolyacid solutions obtained by ion exchange are often relatively dilute so that their concentration is time-consuming.

3. HETEROPOLYSALTS

If the salts cannot be synthesized from their components or cannot be isolated in pure form, they may be conveniently obtained from moderately concentrated solutions of their acids by supersaturation with metal chlorides, or in better yield and

purer form by addition of stoichiometric quantities of the metal carbonate. The carbonate should be added carefully, since an excess will induce decomposition of the heteropolyanion.

REFERENCES:

1. E. Drechsel. Ber. dtsch. chem. Ges. 20, 1452 (1887); A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. 101, 224 (1917).
2. Based on unpublished experiments of G. Jander and D. Ertel; L. C. W. Baker, B. Loev and Th. P. McCutcheon. J. Amer. Chem. Soc. 72, 2374 (1950); R. Klement. Z. anorg. Chem. 260, 267 (1949); F. Hein and H. Lilie. Z. anorg. allg. Chem. 270, 45 (1952).
3. A. Rosenheim and J. Jaenicke. Ibid. 101, 224 (1917); H. Copaux. Ann. Chim. Phys. [8] 17, 217 (1909).

ISOPOLY COMPOUNDS

Isopolyvanadates

1. The Sodium Salt $2Na_2O \cdot V_2O_5 \cdot aq.$

$$\underset{367.9}{2\,Na_3VO_4\,(aq.)} + \underset{200.9}{2\,HClO_4} = \underset{305.9\,*}{2\,Na_2O \cdot V_2O_5\,(aq.)} + \underset{244.9}{2\,NaClO_4}$$

A 1.1M Na_3VO_4 solution is prepared by dissolving V_2O_5 in the stoichiometric quantity of carbonate-free NaOH solution, so that 3 moles of Na are present per mole of V; this corresponds to 100.0 g. of V_2O_5 and 132.0 g. of NaOH per liter. Then, 100 ml. of this solution is acidified by dropwise addition of 24.9 ml. of 4.44N $HClO_4$ (vigorous mechanical stirring). The solution is briefly heated on a steam bath to achieve equilibrium, whereupon the orange liquid becomes colorless. This is then concentrated in vacuum at 25–30°C. The resulting crystals are filtered and washed with some water.

SYNONYM:

Sodium pyrovanadate.

PROPERTIES:

Colorless, water-soluble crystals. Water content: 15 moles of H_2O/mole. In keeping with its molecular weight, should be considered a salt of a divanadic acid $H_4(V_2O_7 \cdot aq.)$.

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*The formula weights given here and subsequently refer to the anhydrous compound.

REFERENCES:

G. Jander and K. F. Jahr, Z. anorg. allg. Chem. 211, 53 (1933); Kolloid-Beihefte 41, 35 (1935).

2. The Sodium Salt $Na_2O \cdot V_2O_5 \cdot aq.$

$$\underset{367.9}{2\,Na_3VO_4\ (aq.)} + \underset{401.9}{4\,HClO_4} = \underset{243.9}{Na_4O \cdot V_2O_5\ (aq.)} + \underset{489.8}{4\,NaClO_4}$$

A 0.812M solution of Na_3VO_4 is prepared as in (1) but using 73.9 g. of V_2O_5 and 97.5 g. of NaOH per liter. Then, 100 ml. of this solution is treated with 57.5 ml. of 2.54N $HClO_4$ (dropwise addition with stirring) and briefly heated on a steam bath until colorless. The mixture is then concentrated in vacuum at 25-30°C. After filtration the crystals are washed with some water.

SYNONYM:

Sodium metavanadate.

PROPERTIES:

Colorless, water-soluble crystals. Water content: 3 moles of H_2O/mole. In keeping with its molecular weight, should be considered a salt of a tetravanadic acid $H_6(V_4O_{13} \cdot aq.)$. Many authors also consider it as the derivative of a trivanadic acid $H_3(V_3O_9 \cdot aq.)$.

REFERENCES:

G. Jander and K. F. Jahr, Z. anorg. allg. Chem. 211, 53 (1933); Kolloid-Beihefte 41, 35 (1935).

3. The Sodium Salt $3\,Na_2O \cdot 5\,V_2O_5 \cdot aq.$

$$\underset{1839.4}{10\,Na_3VO_4\ (aq.)} + \underset{2411.3}{24\,HClO_4} = \underset{1095.5}{3\,Na_2O \cdot 5\,V_2O_5\ (aq.)} + \underset{2868.8}{24\,NaClO_4}$$

The 0.812M Na_3VO_4 solution (150 ml.) is prepared as in (1) and 381 ml. of 0.8M $HClO_4$ is added dropwise with stirring. The mixture is then allowed to stand for about 14 days in a closed flask. At first it becomes dark red, changing to a permanent brighter orange-red in the course of time. It is concentrated in vacuum at 25-30°C. The crystals which form are washed with some water.

PROPERTIES:

Small, hexagonal orange-red platelets with beveled edges, or thin rhombohedra. Grinding changes the crystals into a bright yellow powder. Soluble in H_2O. Water content: 22 moles of H_2O/mole. In keeping with the molecular weight, should be considered as a salt of a pentavanadic acid $H_7(V_5O_{16}\cdot aq.)$ [G. Jander and K. F. Jahr, Kolloid-Beihefte 41, 35 (1935)]. Regarded by many authors as a mixture of salts of different basicity, all of them derivatives of hexavanadic acid $H_4(V_6O_{17}\cdot aq.)$ [see P. Souchay and G. Carpeni, Bull. Soc. Chim. France (5) 13, 160 (1946); A. Rosenheim, Z. anorg. allg. Chem. 96, 139 (1916)].

REFERENCE:

G. Jander and K. F. Jahr, Z. anorg. allg. Chem. 211, 53 (1933).

4. The Potassium Salt $K_2O \cdot 3\ V_2O_5$

This salt is obtained from solutions of commercial potassium "metavanadate" ($1.04\ K_2O \cdot V_2O_5 \cdot 0.78\ H_2O$) by addition of 1.4 moles of acetic acid per mole of vanadate.

Commercial potassium "metavanadate" (7 g.) is dissolved in 25 ml. of water in a beaker placed in a large heating bath (75°C). The hot solution, which is about 2M in vanadium, is then treated with 70 ml. of 1M acetic acid added from a burette whose tip is immersed in the vanadate solution (vigorous mechanical stirring). The acetic acid is introduced at the rate of 1 ml./minute. The red solution is allowed to remain in the heating bath until the latter cools to room temperature (about 15 hours). The clear solution is then cooled to 0°C to induce crystallization. The crystals are filtered off and washed with some ice-cold water, then with acetone.

PROPERTIES:

Formula weight 545.7. Orange-red rhombic crystals or hexagonal platelets, sometimes rather large double pyramids. In view of its chemical behavior and molecular weight, this salt also should be regarded as the salt of pentavanadic acid $H_5(V_5O_{15}\cdot aq.)$. A part of the vanadium is said to be bound cationically, the salt thus having the formula $K_3(VO)[V_6O_{18}]$.

REFERENCE:

K. F. Jahr and G. Jander, Z. anorg. allg. Chem. 220, 204 (1934).

Isopolyniobates

Three types of anions exist in aqueous solutions of alkali niobates; these are in reversible equilibria with each other and their ranges of stability depend on the pH of the solution. All alkali isopolyniobates are salts of the hypothetical hexaniobic acid $H_8Nb_6O_{19}$. The general method of preparation of those salts in which six to eight H^+ are replaced by M^+ consists of fusion of Nb_2O_5 with alkali hydroxide or carbonate, solution of the fused cake in H_2O, and concentration to obtain crystals. The orthoniobate M_3NbO_4 (M = alkali cation) formed in the melt is irreversibly converted to an isopolyniobate by treatment with water. The solubility of the alkali isopolyniobates in water is strongly dependent on the size of the cation. Thus, Li and Na salts invariably dissolve with difficulty (especially in the presence of excess Li^+ or Na^+), while K, Rb and Cs salts are readily to very readily soluble. The solutions are strongly alkaline. All alkali niobate solutions are very sensitive to acids; even small amounts of mineral acids produce irreversible clouding of the solutions or precipitates of $Nb_2O_5 \cdot aq.$ On heating to over 300°C, all alkali isopolyniobates lose water irreversibly to give the anhydrous, insoluble alkali metaniobates $MNbO_3$.

$M_8[Nb_6O_{19} \cdot aq.]$ or $4M_2O \cdot 3Nb_2O_5 \cdot aq.$ (8:6 type)

$$8\,MOH + 3\,Nb_2O_5 = 6\,M_3NbO_4 + 9\,H_2O \text{ (fusion)}$$

$$6\,M_3NbO_4 + 5\,H_2O = M_8[Nb_6O_{19} \cdot aq.] + 10\,MOH$$

To prepare the K salt, Nb_2O_5 and KOH (mole ratio ~1:20, weight ratio ~4:17) are heated in a silver or alumina crucible until a clear melt is obtained. The melt is cooled, ground and dissolved in H_2O. The solution is decanted to remove any insoluble matter which may be present, then concentrated in vacuum over conc. H_2SO_4 until formation of crystals. These are washed with some water and dried on filter paper.

The corresponding Na salt is obtained from aqueous solutions of the K salt by treatment with NaOH (stirring). The fine, crystalline, white precipitate is filtered off, washed with water, alcohol and ether, and dried.

PROPERTIES:

Well-crystallized salts; the water content varies somewhat depending on the method of preparation. The large, transparent crystals of the K salt effloresce when stored under sharply desiccating conditions; they then become cloudy, but retain their good solubility in water.

DropBooks

Depending on the conditions of precipitation (hot or ice-cold solutions), the 8:6 sodium salt gives differing crystalline forms (needles or leaflets), which also differ in their water content.

In aqueous solutions, salts of the type $M_8[Nb_6O_{19} \cdot aq.]$ are stable only at pH > 13.

$M_7[HNb_6O_{19} \cdot aq.]$ or $7M_2O \cdot 6Nb_2O_5 \cdot aq.$ (7:6 type)

$$M_8[Nb_6O_{19} \cdot aq.] + H_2O = M_7[HNb_6O_{19} \cdot aq.] + MOH$$

Two recrystallizations of the 8:6 sodium salt from H_2O afford $Na_7[HNb_6O_{19} \cdot aq.]$.

Another method of preparation starts with the fusion of Nb_2O_5 with Na_2CO_3 (mole ratio ~ 1:4, weight ratio ~ 5:8); the cooled melt is ground, treated with a large amount of H_2O, and stirred for several hours. Since the solubility of sodium niobate is poor, only the excess Na_2CO_3 dissolves in this operation. The residue is recrystallized from H_2O to give pure 7:6 sodium niobate.

The corresponding K salt is best prepared by addition of alcohol to solutions which contain 10 weight percent or more of pure 8:6 potassium niobate.

PROPERTIES:

The 7:6 sodium niobate forms long crystalline needles; water content: 32 moles of H_2O/mole.

The 7:6 potassium niobate precipitated with alcohol readily loses its water of crystallization and forms lower hydrates; e.g., at 100°C, it gives the penta- or tetrahydrate, and at 150°C, the dihydrate.

In aqueous solutions, salts of the type $M_7[HNb_6O_{19} \cdot aq.]$ are stable only in the pH range of 9 to 13.

$(M_6[Nb_6O_{18} \cdot aq.])_n$ or $(6M_2O \cdot 6Nb_2O_5 \cdot aq.)_n$ (6:6 type)

$$nM_7[HNb_6O_{19} \cdot aq.] + nH_2O = (M_6[Nb_6O_{18} \cdot aq.])_n + nMOH$$

A 2-4% aqueous solution of 8:6 potassium niobate (or a concentrated solution of 7:6 potassium niobate) is treated by dropwise addition of an equal volume of methyl alcohol (cooling in ice, vigorous mechanical stirring). The product is an amorphous, flocculent hydrated potassium niobate.

It is filtered, washed with 50% methyl alcohol, and dried under mild conditions.

PROPERTIES:

Pure white powder. Readily soluble in water. The water content varies depending on the conditions of preparation. The hydrated

metaniobate is stable only in aqueous solutions of pH < 8 (probably as far as the region of the isoelectric point, which occurs at pH ~4.5). At higher pH values, changes first to the 7:6 type (pH 9–13), and then to the 8:6 type (pH > 13). Based on diffusion measurements, the anion $([Nb_6O_{19} \cdot aq.]^{8-})_n$ has an ionic weight ~3000 (n = 3–4), so that the designation in the heading of this section is preferred to the formulas $M_2O \cdot Nb_2O_5 \cdot aq.$ or $MNbO_3 \cdot aq.$ which are sometimes encountered.

REFERENCES:

G. Jander and D. Ertel, J. Inorg. Nuclear Chem. 14, 71, 77, 85 (1960); A. V. Lapitskiy and V. I. Spitsyn, Zh. Prikl. Khim. 26, 101 (1953); F. Windmaisser, Österr. Chemiker-Ztg. 45, 201 (1942); P. Süe, Ann. Chimie [11] 7, 493 (1937).

Isopolytantalates

As far as the general method of preparation of alkali isopolytantalates, their water solubility and their thermal behavior are concerned, the introductory remarks made in the section on isopolyniobates apply here as well. However, the composition of the alkali isopolytantalates, i.e., the base:acid ratio, is not yet completely clear. While some authors find hexatantalates (8:6) exclusively, others have established that only pentatantalates (7:5) exist, and still others insist that both types of compounds occur together, and are possibly related to each other via a region in which only one exists.

For this reason, we have given here several procedures taken from the original references.

$K_7[Ta_5O_{16} \cdot aq.]$ or $7K_2O \cdot 5Ta_2O_5 \cdot aq.$ (pentatantalate, 7:5 type)
$K_8[Ta_6O_{19} \cdot aq.]$ or $4K_2O \cdot 3Ta_2O_5 \cdot aq.$ (hexatantalate, 8:6 type)

Either Ta_2O_5 and KOH (mole ratio ~1:20, weight ratio ~2:5), or Ta_2O_5 and K_2CO_3 (mole ratio ~1:4) are heated in a silver or alumina crucible (or a platinum vessel) until a clear melt is obtained. The melt is cooled, ground and dissolved in H_2O. The solution is decanted from any insoluble matter and concentrated in vacuum over conc. H_2SO_4 until crystallization occurs. The crystals are rinsed with H_2O and dried on filter paper. Their crystal size increases with the excess alkali hydroxide or carbonate present in the mother liquor.

PROPERTIES:

Hexagonal prismatic columns up to 1 cm. long, with sharp edges; effloresce when stored under sharply desiccating conditions.

Readily soluble in water, giving a strong alkaline reaction. The content of water of crystallization varies.

REFERENCES:

G. Jander and H. Schulz. Z. anorg. allg. Chem. 144, 233 (1925); G. Jander and D. Ertel. J. Inorg. Nuclear Chem. 3, 139 (1956); F. Windmaisser. Z. anorg. allg. Chem. 248, 283 (1941).

$Na_7[Ta_5O_{16} \cdot aq.]$ or $7Na_2O \cdot 5Ta_2O_5 \cdot aq.$ (pentatantalate)

A mixture of Ta_2O_5 and NaOH (mole ratio 1:5, weight ratio 11:5) is melted. The melt is cooled, ground, dissolved in H_2O and treated in the cold (stirring) with 0.1N NaOH. Pure white Na pentatantalate precipitates. It is washed with H_2O, alcohol and ether, and dried. Sodium pentatantalate also forms when the aqueous solution of the melt is evaporated at 85°C.

Alternate method: The same salt is obtained by treatment of a hot potassium tantalate solution with hot aqueous NaOH.

PROPERTIES:

Small prismatic needles; d^{20} 3.78. Water content: 22 moles of H_2O/mole; moderately soluble in water. The pH of a 1% solution is 8.48.

REFERENCES:

V. I. Spitsyn and N. N. Shavrova. Zh. Obshch. Khim. 26, 1258 (1956); G. Jander and D. Ertel. J. Inorg. Nuclear Chem. 3, 139 (1956).

$Na_8[Ta_6O_{19} \cdot aq.]$ or $4Na_2O \cdot 3Ta_2O_5 \cdot aq.$ (hexatantalate)

The melt obtained by fusion of Ta_2O_5 and NaOH (mole ratio 1:5, weight ratio 11:5) is cooled, ground and treated with ten times its weight of cold H_2O to remove excess alkali. The residue is dissolved in H_2O at 80°C and concentrated at 50°C.

PROPERTIES:

Small leaflets; d^{20} 3.58. Water content: 33 moles of H_2O/mole; moderately soluble in water; pH of a 1% solution = 8.58. Goniometric measurements indicate that this Na hexatantalate belongs to the hexagonal system.

REFERENCES:

V. I. Spitsyn and N. N. Shavrova, Zh. Obshch. Khim. 26, 1256, 1262 (1956).

Isopolyarsenates

Sodium Hydrogen Triarsenate $Na_3H_2As_3O_{10}$

$$3\,NaH_2AsO_4 \cdot H_2O \rightarrow Na_3H_2As_3O_{10} + 5\,H_2O$$
545.8 (incl. H_2O) 455.7 90.1

This salt is formed on dehydration of $NaH_2AsO_4 \cdot H_2O$. Very slow heating of the starting material yields several intermediate products (NaH_2AsO_4 and $Na_2H_2As_2O_7$), which transform above 135°C to the triarsenate $Na_3H_2As_3O_{10}$. The last is stable up to 230°C. Rapid heating of the starting $NaH_2AsO_4 \cdot H_2O$ to temperatures above 96°C yields the triarsenate directly.

The best method of preparation is to place about 10 g. of $NaH_2AsO_4 \cdot H_2O$ (see p. 602) in a weighing bottle and heat it to constant weight (about 25 hours) in an electric furnace at 135°C.

DropBooks

PROPERTIES:

Absorbs H_2O from air at room temperature; after several intermediate stages, $NaH_2AsO_4 \cdot H_2O$ is finally regenerated. Immediately hydrated to the orthoarsenate upon solution in water. Considered by Thilo and Plaetschke to be the doubly acid salt of the pentabasic triarsenic acid $H_5As_3O_{10} = As_2O_5 \cdot {}^5/_3\,H_2O$. For the preparation of $As_2O_5 \cdot {}^5/_3\,H_2O$, see this handbook, p. 601.

REFERENCE:

E. Thilo and I. Plaetschke, Z. anorg. Chem. 260, 315 (1949).

Isopolychromates

Potassium Trichromate $K_2O \cdot 3CrO_3$

This salt is formed on careful evaporation of an aqueous solution of $K_2Cr_2O_7$ and excess CrO_3.

A solution of 11.0 g. of $K_2Cr_2O_7$ and 17.4 g. of CrO_3 (mole ratio $K_2O:CrO_3 = 1:6.66$) in 22.0 ml. of water is prepared at 60°C, a temperature at which the solution is saturated. Evaporation at 60°C yields deep red crystals. The liquid is evaporated to

13 ml. and then decanted rapidly while still warm. The crystals are dried by pressing on filter paper. Yield: about 7.8 g.

PROPERTIES:

Formula weight 394.2. Deep red prisms, containing no water of crystallization; decomposes on solution in water. Stable in solutions only in the presence of excess CrO_3 or conc. HNO_3.

Potassium Tetrachromate $K_2O \cdot 4CrO_3$

This salt is obtained from aqueous solutions of $K_2Cr_2O_7$ in the presence of a large excess of CrO_3. The evaporation should not be carried too far.

A saturated solution of 15.67 g. of $K_2Cr_2O_7$ and 43.43 g. of CrO_3 (mole ratio $K_2O:CrO_3 = 1:10.15$) in 40.9 ml. of water is prepared at 60°C and concentrated at this temperature to about 10 ml. The nascent crystals are separated and dried as described in the case of the trichromate. Yield: about 13 g.

PROPERTIES:

Formula weight 494.2. Brownish red tablets, containing no water of crystallization; decomposes on solution in water. Stable in solutions only in the presence of excess CrO_3 or conc. HNO_3.

REFERENCES:

E. Jäger and G. Krüss. Ber. dtsch. chem. Ges. 22, 2040 (1889); F. A. H. Schreinemakers. Z. phys. Chem. 55, 71 (1906). Checked by the present authors.

Isopolymolybdates

The compounds described below should be considered derivatives of a hexamolybdic acid $H_6(Mo_6O_{21} \cdot aq.)$ [see G. Jander and K. F. Jahr, Kolloid-Beihefte 41, 27 (1935)].

The Sodium Salt $5Na_2O \cdot 12MoO_3 \cdot aq.$

$$\underset{1727.4}{12\,MoO_3} + \underset{400.0}{10\,NaOH} = \underset{2037.3}{5\,Na_2O \cdot 12\,MoO_3\,(aq.)}$$

Sodium hydroxide (8 g.) is dissolved in 100 ml. of hot H_2O, and 20 g. of MoO_3 is added. The pH of the cooled, clear solution (filtered, if necessary) is about 5. It is evaporated in a vacuum

desiccator over H_2SO_4 to 3/4 to 2/3 of its original volume. The compound precipitates in the form of a slurry, which is filtered and washed with some H_2O.

SYNONYM:

Sodium paramolybdate.

PROPERTIES:

According to Rosenheim, large, lustrous monoclinic prisms which effloresce easily. Water content: 38 moles of H_2O/mole. Soluble in H_2O. In our own experiments, evaporation in vacuum or on a steam bath gave a granular white mass, which was not significantly soluble in water either after drying or when freshly prepared and moist.

REFERENCE:

A. Rosenheim. Z. anorg. allg. Chem. 96, 143 (1916). Checked by the present authors.

DropBooks

The Ammonium Salt $5(NH_4)_2O \cdot 12MoO_3 \cdot aq$.

The reaction vessel is a porcelain dish. It contains 20 g. of MoO_3, covered with 230 ml. of conc. ammonia. The solution is gently evaporated on a steam bath (solution temperature 60-70°C) until the excess NH_3 is removed and the first crystals form (this occurs upon concentration to about 1/5 of the original volume). The concentrate is cooled and the crystals are filtered off. Yield: about 20 g.

PROPERTIES:

Formula weight 1987.8. According to Rosenheim, large, clear, colorless hexagonal prisms, moderately soluble in H_2O. Water content: 7 moles of H_2O/mole. This product is the ammonium molybdate of commerce. Its aqueous solution gives an acid reaction and the compound undergoes hydrolytic cleavage on prolonged boiling. Our own experiments yielded small, white crystals, soluble in hot H_2O.

REFERENCE:

A. Rosenheim. Z. anorg. allg. Chem. 96, 143 (1916). Checked by the present authors.

The Sodium Salt $Na_2O \cdot 4MoO_3 \cdot aq.$

$$\underset{523.8}{4\,Na_2MoO_4\,(aq.)} + \underset{218.8}{6\,HCl} = \underset{637.8}{Na_2O \cdot 4\,MoO_3\,(aq.)} + \underset{350.7}{6\,NaCl}$$

A solution of 9.3 g. of $Na_2MoO_4 \cdot 2\,H_2O$ in about 8 ml. of hot H_2O is treated, while still hot, with 11 ml. of 5.5N HCl added dropwise from a burette. The initial precipitate redissolves, giving a yellowish solution. The liquid, in a stoppered Erlenmeyer flask, is left in a cool place to crystallize. A crystalline crust appears after 24 hours and its thickness increases in the course of the next few days. The crystals are filtered off, washed three times with cold water, and dried by drawing air through the crystal layer. Yield: 6 g.

SYNONYM:

Sodium metamolybdate.

PROPERTIES:

Relatively long needles, partially pulverized when touched. Moderately soluble in cold H_2O, very soluble in hot. Water content: 6 moles of H_2O/mole.

REFERENCE:

G. Wempe, Z. anorg. Chem. 78, 302 (1912). Checked by the present authors.

Isopolytungstates

The compounds described below are derivatives of a hexatungstic acid $H_6(W_6O_{21} \cdot aq.)$ [see G. Jander and K. F. Jahr, Kolloid-Beihefte 41, 18 (1935)].

The Sodium Salt $5Na_2O \cdot 12WO_3 \cdot aq.$

$$\underset{3526.9}{12\,Na_2WO_4\,(aq.)} + \underset{510.8}{14\,HCl} = \underset{3098.0}{5\,Na_2O \cdot 12\,WO_3\,(aq.)} + \underset{818.3}{14\,NaCl}$$

A solution of 20 g. of $Na_2WO_4 \cdot 2\,H_2O$ in 40 ml. of hot H_2O is neutralized to litmus with 2N HCl. About 23.5 ml. of HCl is required (about 1.2 moles of HCl per mole of Na_2WO_4). The pH of the solution is then 6.8. The salt is allowed to crystallize in a vacuum desiccator at room temperature over H_2SO_4.

SYNONYM:

Sodium paratungstate.

PROPERTIES:

Large transparent or milky-white triclinic crystals. Water content: 28 moles of H_2O/mole. Readily soluble in water. Other hydrates exist at higher temperatures. The recent views on the complex processes involved in the formation of paratungstates are given by Jander and Krüerke.

REFERENCES:

A. Rosenheim. Z. anorg. allg. Chem. 96, 160 (1916); C. Scheibler. J. prakt. Chem. 83, 284 (1861). Checked by the present authors. G. Jander and U. Krüerke. Z. anorg. allg. Chem. 265, 244 (1951).

The Ammonium Salt $5(NH_4)_2O \cdot 12WO_3 \cdot aq.$

Hydrated tungstic acid is dissolved in excess ammonia, and the solution is concentrated on a steam bath or at room temperature, whereby the excess ammonia evaporates.

DropBooks

SYNONYM:

Ammonium paratungstate.

PROPERTIES:

Formula weight 3042.72. Microscopically small, rectangular tablets when the solution is evaporated at high temperatures. Water content: 7 moles of H_2O/mole. A different hydrate exists at room temperature and below. Rather sparingly soluble in H_2O. On prolonged boiling in aqueous solution, the salt is hydrolytically decomposed and loses NH_3.

REFERENCE:

A. Rosenheim. Z. anorg. allg. Chem. 96, 158 (1916).

The Zinc Salt $5ZnO \cdot 12WO_3 \cdot aq.$

$$5\,Na_2O \cdot 12\,WO_3\,(aq.) + 5\,ZnSO_4 = 5\,ZnO \cdot 12\,WO_3\,(aq.) + 5\,Na_2SO_4$$

3093.01 807.2 3189.94 7103.

A solution is prepared by heating a mixture of 7.8 g. of sodium paratungstate (prepared as above) and 70 ml. of water. The mixture is then reacted with a warm, saturated solution of

$ZnSO_4 \cdot 7\,H_2O$ in 15 ml. of water. A white precipitate forms, partially redissolves, and then settles out. It is suction-filtered and dried over conc. H_2SO_4.

SYNONYM:

Zinc paratungstate.

PROPERTIES:

White needles or fine, crystalline precipitate; poor solubility in H_2O. Water content: 35 moles of H_2O/mole.

REFERENCE:

A. Rosenheim, Z. anorg. allg. Chem. 96, 162 (1916). Checked by the present authors.

Isopolysulfates

Potassium Trisulfate $K_2S_3O_{10}$

I. $$K_2SO_4 + 2SO_3 = K_2S_3O_{10}$$
174.3 160.1 334.4

According to Baumgarten and Thilo, $K_2S_3O_{10}$ may be prepared from K_2SO_4 by treatment with SO_3. The apparatus used is shown in Fig. 342.

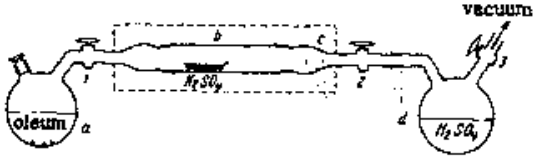

Fig. 342. Preparation of potassium trisulfate. *a* flask with oleum; *b* reactor tube, here shown surrounded by an electric tubular furnace; *d* flask with conc. H_2SO_4; *1-3* stopcocks. The reactor tube *c* is longer in relation to other parts of the apparatus than shown.

All parts of the glass apparatus are connected by ground joints. The joints are sealed with a paste made from 10 g. of powdered talc (preboiled several times in HCl) and 14 g. of anhydrous phosphoric acid. Stopcock plugs 1 and 2 should be of as large a

diameter as possible; stopcock 3 may be of normal size. After thorough drying of all parts of the apparatus a boat of quartz, glazed porcelain, or platinum containing finely powdered, ignited K_2SO_4 is inserted into reaction tube *b*; following this, adapter *c* and flask *d* (containing 96.5% H_2SO_4) are attached. Stopcock 1 is closed, and the section *b*–*d* is evacuated with an aspirator. Stopcock 3 is then closed, and the apparatus is left to dry for a while. Flask *a* is then filled with 70% oleum, a few glass beads are added, stopcock 1 is reopened, and the entire apparatus is rapidly evacuated with the aspirator, so that the oleum evolves. Stopcocks 2 and 3 are then closed. The flask containing the oleum is heated to about 110°C in a sulfuric acid bath until enough SO_3 distills and condenses in tube *b* to entirely surround the boat with the liquid. Flask *a* is then allowed to cool somewhat and stopcock 1 is closed. Tube *b* (between 1 and 2) is heated externally to 50–53°C, using a sheet iron heating trough lined with asbestos, and covering the top with asbestos. The trough is heated with a row burner, while the stopcocks and flasks are insulated with asbestos to prevent heating. The 50–53°C temperature desired is measured in the space between the reactor tube and the trough. Alternatively, an electric furnace may be used, as shown in the figure.

In the next two hours, the K_2SO_4 will sinter, become a slurry and finally convert to a clear liquid. If the quantity of SO_3 present is insufficient, the melt may resolidify. At the end of the reaction, stopcock 2 is reopened, flask *d* is cooled in ice, and the excess SO_3 is distilled onto the cooled H_2SO_4, first at room temperature and finally by heating the reaction tube two hours at 100°C. The apparatus is allowed to cool and stopcock 3 is opened; little or no fuming should then occur.

Propbooks

II.
$$\underset{277.1}{2\,KClO_4} + \underset{240.2}{3\,SO_3} = \underset{334.4}{K_2S_3O_{10}} + \underset{182.9}{Cl_2O_7}$$

According to Lehmann and Krüger, the reaction of SO_3 with $KClO_4$ produces potassium trisulfate and Cl_2O_7; the latter dissolves in the excess SO_3. The residue obtained on vacuum evaporation of the excess SO_3 and the Cl_2O_7 is chlorine-free, stoichiometric $K_2S_3O_{10}$.

Extremely dry, fine $KClO_4$ powder, free of reducing impurities, is placed in the apparatus of Baumgarten and Thilo shown in Fig. 342 and treated with SO_3-free SO_3 at 25–30°C until the contents of the boat become completely liquid. Excess SO_3 and Cl_2O_7 are then absorbed in conc. H_2SO_4 at room temperature, while vacuum is applied at 3.

PROPERTIES:

According to recent studies, $K_2S_3O_{10}$ is thermally stable up to 110°C. Above this temperature the vapor pressure of SO_3 begins

to increase and the compound decomposes into potassium pyrosulfate and SO_3. The $K_2S_3O_{10}$ prepared by the method of Baumgarten and Thilo is a cake which can readily be ground to a fine powder. It absorbs water from the air and converts to an adduct of sulfuric acid and pyrosulfate or hydrogen sulfate. It decomposes immediately (with fizzing) in cold water; in the first stage of decomposition, only 1 mole of SO_3 is evolved and a pyrosulfate of relatively poor solubility is formed.

REFERENCES:

P. Baumgarten and E. Thilo. Ber. dtsch. chem. Ges. 71, 2596 (1938); H. A. Lehmann and G. Krüger. Z. anorg. allg. Chem. 274, 141 (1973); H. A. Lehmann and A. Kluge. Ibid. 264, 120 (1951).

HETERPOLY COMPOUNDS

12-Tungstic Acid-1-Borates

In keeping with their constitution and molecular weight, these compounds should be regarded as salts of 12-tungstic-1-boric acid $H_5[BO_4(W_3O_9)_4 \cdot aq.]$ [R. Signer and H. Gross, Helv. Chim. Acta 17, 1076 (1934)].

The Free Acid $B_2O_3 \cdot 24WO_3 \cdot aq.$

The first step involves the preparation of a solution of $5\,Na_2O \cdot B_2O_3 \cdot 24\,WO_3 \cdot aq.$ from $Na_2WO_4 \cdot aq.$ and H_3BO_3. A large excess of boric acid is used to bind the alkali of the Na_2WO_4 and to ensure that the solution remains acidic. The acid can be isolated from the solution of the sodium salt by addition of ether and sulfuric acid according to the method of Drechsel (see p. 1700 f.).

A solution of 100 g. of $Na_2WO_4 \cdot 2\,H_2O$ and 150 g. of H_3BO_3 is prepared in 400–500 ml. of boiling H_2O. The solution is boiled until a sample deposits no tungstic acid when dil. HCl is added. The solution is cooled, suction-filtered to remove the boric acid and sodium polyborate crystals, reacted again with 70 g. of H_3BO_3, and concentrated over a free flame. The crystalline mass which separates on cooling is again filtered off and washed with some 33% H_2SO_4. The mother liquor, which contains $5\,Na_2O \cdot B_2O_3 \cdot 24\,WO_3 \cdot aq.$, is extracted with 2–3 volumes of 33% H_2SO_4 and ether according to the method of Drechsel. For further workup see p. 1701.

PROPERTIES:

Formula weight 5634.3. Two forms:

a) Perfectly clear octahedral crystals, initially bright but acquiring a greasy luster and a yellowish cast on storage; otherwise, can be stored for a long time. Water content: 65 or 66 moles of H_2O/mole. M.p. 45–51°C. Soluble in water.

b) Hexagonal needles, less stable, more apt to become yellow and cloudy. Water content: 53 moles of H_2O/mole. Soluble in H_2O. The m.p. cannot be determined, since heating causes decomposition. These crystals were formerly thought to be those of an isoborotungstic acid.

REFERENCE:

A. Rosenheim and J. Jaenicke, Z. anorg. Chem. 77, 244 (1912); 101, 236 (1917).

The Sodium Salt $5Na_2O \cdot B_2O_3 \cdot 24WO_3 \cdot aq.$

The crystalline sodium salt is best prepared from the free acid by addition of the stoichiometric quantity of Na_2CO_3.

$$\underset{5635.7}{B_2O_3 \cdot 24WO_3(aq.)} + 5\,\underset{530.0}{Na_2CO_3} = \underset{5945.7}{5Na_2O \cdot B_2O_3 \cdot 24WO_3(aq.)} + 5\,CO_2$$

DropBooks

A solution containing 34.4 g. of free 12-tungstic-1-boric acid (equivalent to about 41.6 g. of the hydrated acid) is reacted with 3.1 g. of anhydrous Na_2CO_3, and concentrated first on a steam bath and then in a desiccator over conc. H_2SO_4.

PROPERTIES:

White, well-formed octahedra. Soluble in H_2O. Water content: 58 moles of H_2O/mole.

REFERENCE:

A. Rosenheim and H. Schwer, Z. anorg. Chem. 89, 236 (1914).

12-Tungstic Acid-1-Silicates

In view of their structure and molecular weight, all compounds of this type should be considered as salts of 12-tungstic-1-silicic acid $H_4[SiO_4(W_3O_9)_4 \cdot aq.]$ {R. Signer and H. Gross, Helv. Chim. Acta 17, 1076 (1934)}.

The Free Acid $SiO_2 \cdot 12WO_3 \cdot aq.$

$$12\,Na_2WO_4\,(aq) + SiO_2 + 20\,HCl = 2\,Na_2O \cdot SiO_2 \cdot 12\,WO_3\,(aq.) + 20\,NaCl$$
$$3336.9 \qquad 60.06 \qquad 729.4 \qquad 2967.1 \qquad 1169.0$$

The free acid is isolated from a solution of $2\,Na_2O \cdot SiO_2 \cdot 12\,WO_3 \cdot aq.$ by the method of Drechsel, that is, extraction with ether and conc. HCl.

A solution of 50 g. of $Na_2WO_4 \cdot 2\,H_2O$ in 400 ml. of cold H_2O is prepared. It is then treated by dropwise addition of about 27 ml. of 6N HCl, until neutral to litmus. The white precipitate formed during the addition redissolves on swirling the flask. An excess of freshly precipitated silicic acid hydrate is now added to the solution. (The silicic acid is prepared as follows. Commercial sodium silicate is dissolved in a minimum of cold H_2O and made neutral to litmus by dropwise addition of conc. HCl. After 15 minutes a small excess of acid is added. The solution is decanted and the precipitate is washed once or twice with cold water, which is likewise decanted.)

The mixture of tungstate and silicic acid is boiled for about two hours (the liquid being kept acidic by periodic addition of small amounts of HCl) until a filtered sample of the solution no longer precipitates tungstic acid hydrate on addition of dil. HCl. The solution is filtered to remove undissolved SiO_2 and shaken with ether and conc. HCl. For further workup, see p. 1701. If the free acid is to be used only as starting material for preparation of a salt, the oily adduct may be decomposed at about 40°C, the ether removed by long heating, and the excess hydrochloric acid removed by drawing air through the slowly solidifying residue. The yield is 27 g.; the product is not completely pure.

PROPERTIES:

Formula weight 2842.4. The acid crystallizes at room temperature in colorless, lustrous octahedra; m.p. 53°C. Water content: 32 moles of H_2O/mole. Readily soluble in H_2O. Several different crystalline hydrates exist, one of which is denoted the "iso acid."

REFERENCE:

A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. 101, 240 (1917). Checked by the present authors.

The Potassium Salt $2K_2O \cdot SiO_2 \cdot 12WO_3 \cdot aq.$

$$SiO_2 \cdot 12\,WO_3\,(aq.) + 2\,K_2CO_3 = 2\,K_2O \cdot SiO_2 \cdot 12\,WO_3\,(aq.) + 2\,CO_2$$
$$2843.1 \qquad 276.4 \qquad 3091.5$$

An aqueous solution of the free acid (about one part by weight of acid to three or four parts of H_2O), whose content is determined

by evaporation and ignition of an aliquot, is treated by slow addition of the stoichiometric quantity of solid K_2CO_3 (two moles of K_2CO_3 per mole of acid) while applying heat. The clear solution, which must retain an acidic reaction, is evaporated on a steam bath to 1/2 to 1/4 its volume. Cooling precipitates $2\ K_2O \cdot SiO_2 \cdot 12\ WO_3 \cdot aq.$, first in hexagonal prisms and then also as rhombic crystals. The product is recrystallized from hot H_2O.

PROPERTIES:

The hexagonal, colorless prisms effloresce easily. Water content: 18 moles of H_2O/mole. Readily soluble in hot H_2O, somewhat less so in cold. The rhombic crystals are said to be the salt of the so-called "iso acid"; they do not effloresce so rapidly. Water content: 9 moles of H_2O/mole.

REFERENCE:

A. Rosenheim and J. Jaenicke, Z. anorg. allg. Chem. 101, 243 (1917). Checked by the present authors.

10-Tungstic Acid-1-Silicates

The Potassium Salt $7K_2O \cdot 2SiO_2 \cdot 20WO_3 \cdot aq.$

This salt is obtained by careful decomposition of a 12-tungstic acid-1-silicate with K_2CO_3.

A solution of 8 g. of $2\ K_2O \cdot SiO_2 \cdot 12\ WO_3 \cdot aq.$ in a minimum of H_2O is prepared at room temperature and treated carefully (no heating) with a fairly conc. solution of K_2CO_3 in H_2O (2 moles of K_2CO_3 = 276.4 g. per mole of $2\ K_2O \cdot SiO_2 \cdot 12\ WO_3$; one mole of the compounds containing 18 or 9 moles of H_2O/mole weight 3355.8 or 3193.6 g., respectively). At this point, the solution gives a neutral reaction, and the desired potassium salt crystallizes out immediately with no need for further concentration. The salt is washed with some cold water. Yield: 4.5 g.

PROPERTIES:

Formula weight 5416.78. Sparkling crystals. Water content: 23 moles of H_2O/mole.

REFERENCE:

F. Kehrmann, Z. anorg. Chem. 39, 103 (1904). Checked by the present authors.

DropBooks

12-Tungstic Acid-1-Phosphates

In keeping with their molecular weight and constitution, these compounds should be regarded as derivatives of a 12-tungstic-1-phosphoric acid $H_3[PO_4(W_3O_9)_4 \cdot aq.]$ [J. F. Keggin, Proc. Roy. Soc. A 144, 75 (1934)].

The Sodium Salt $3Na_2O \cdot P_2O_5 \cdot 24WO_3 \cdot aq.$

$$\underset{7053.6}{24\,Na_2WO_4\,(aq.)} + \underset{284.0}{2\,Na_2HPO_4} + \underset{1077.6}{46\,HCl} = \underset{5894.0}{3\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3\,(aq.)} + \underset{2688.7}{46\,NaCl}$$

A solution of 50 g. of $Na_2WO_4 \cdot 2\,H_2O$ and 25 g. of $Na_2HPO_4 \cdot 12\,H_2O$ in 80 ml. of H_2O is evaporated until a surface skin of crystals forms; then 75 ml. of 24% HCl (d 1.12) is added with stirring. A precipitate forms momentarily, but then redissolves completely. The solution is reevaporated on a steam bath until a crystal skin begins to form. The product is recrystallized from H_2O.

PROPERTIES:

Large colorless (sometimes slightly greenish) columnar crystals. Water content: 30 moles of H_2O/mole. Another hydrate also exists. Soluble in H_2O.

REFERENCE:

A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. 101, 251 (1917). Checked by the present author.

The Free Acid $P_2O_5 \cdot 24WO_3 \cdot aq.$

This salt is obtained by Drechsel's method (p. 1700), that is, by extracting a solution of $3\,Na_2O \cdot P_2O_6 \cdot 24\,WO_3 \cdot aq.$ with ether and conc. HCl. Light yellow or greenish crystals precipitate. However, if the starting sodium salt is first recrystallized once or twice, the product consists of transparent, colorless crystals.

This acid is also prepared very readily by ion exchange (see p. 1701). The starting solution contains 20 g. of $3\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot aq.$ in 100 ml. of H_2O. The colorless eluate is concentrated in a vacuum desiccator. Yield: 11 g.

PROPERTIES:

Formula weight 5706.59. The colored crystals disintegrate, often even in a few hours, to a crystalline powder; the colorless

crystals may often be kept for months. Large, lustrous octahedra, soluble in H_2O. Water content: 63 moles of H_2O/mole. This hydrate readily converts to a hydrate with 51 moles of H_2O/mole, which forms trigonal crystals and begins to melt at 89°C. It loses its water of crystallization in a vacuum desiccator over H_2SO_4.

REFERENCES:

A. Rosenheim and J. Jaenicke, Z. anorg. allg. Chem. 101, 251 (1917); G. Jander and D. Ertel, unpublished experiments.

The Potassium Salt $3K_2O \cdot P_2O_5 \cdot 24WO_3 \cdot aq.$

The Ammonium Salt $3(NH_4)_2O \cdot P_2O_5 \cdot 24WO_3 \cdot aq.$

$$\underset{5894.0}{3\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3\,(aq.)} + \underset{447.3}{6\,KCl}\ [\underset{321.0}{6\,NH_4Cl}]$$

$$= \underset{5990.6}{3\,K_2O \cdot P_2O_5 \cdot 24\,WO_3\,(aq.)}\ [\underset{5864.3}{3\,(NH_4)_2O \cdot P_2O_5 \cdot 24\,WO_3\,(aq.)}] + \underset{350.7}{6\,NaCl}$$

A solution of the free acid $P_2O_5 \cdot 24\,WO_3 \cdot aq.$ or the sodium salt $3\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot aq.$ is treated with KCl or NH_4Cl. A thick white precipitate forms, even if the solutions are very dilute and contain free mineral acids.

DropBOOKS

PROPERTIES:

Microcrystalline white precipitates, which filter with difficulty. Very poor solubility in H_2O.

REFERENCE:

F. Kehrmann and M. Freinkel, Ber. dtsch. chem. Ges. 24, 2326 (1891). Checked by the present authors.

The Barium Salt: $3BaO \cdot P_2O_5 \cdot 24WO_3 \cdot aq.$

$$\underset{5894.0}{3\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3\,(aq.)} + \underset{624.8}{3\,BaCl_2} = \underset{6168.1}{3\,BaO \cdot P_2O_5 \cdot 24\,WO_3\,(aq.)} + \underset{350.7}{6\,NaCl}$$

A saturated solution of 14 g. of $3\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot aq.$ is mixed, while hot, with 60 ml. of hot, saturated $BaCl_2$ solution. The liquid becomes cloudy, and a heavy, white crystalline precipitate forms on cooling. Concentration of the mother liquor (not too far) gives a second fraction of the desired barium salt. Yield: about 7 g.

PROPERTIES:

Well-formed, regular, colorless octahedra, which effloresce in air. Water content: 58 moles of H_2O/mole. Moderately soluble in H_2O.

REFERENCE:

F. Kehrmann and M. Freinkel, Ber. dtsch. chem. Ges. 24, 2326 (1891). Checked by the present authors.

22-Tungstic Acid-2-Phosphates

The Potassium Salt $7K_2O \cdot P_2O_5 \cdot 22WO_3 \cdot aq.$

Produced by careful decomposition of a 12-tungstic acid-1-phosphate with K_2CO_3.

An approximately 30% suspension of $3\,K_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot aq.$ in water is heated to boiling and treated with about 10% K_2CO_3 solution until solution is complete. Excess K_2CO_3 should be avoided. The solution, which then has a neutral reaction, is evaporated on the steam bath. On cooling, $7\,K_2O \cdot P_2O_5 \cdot 22\,WO_3 \cdot aq.$ separates out. It may be recrystallized from H_2O which contains some acetic acid.

PROPERTIES:

Formula weight 5902.3. Large, octahedral crystals, partially present as spearlike aggregates, accompanied by a fine powder. Soluble in hot water, less so in cold. Decomposes in the presence of free mineral acid (see next preparation).

REFERENCES:

F. Kehrmann, Z. anorg. Chem. 1, 435 (1892); P. Souchay, Ann. Chimie [12] 2, 204 (1947). Checked by the present authors.

21-Tungstic Acid-2-Phosphates

The Potassium Salt $3K_2O \cdot P_2O_5 \cdot 21WO_3 \cdot aq.$

Produced from $7\,K_2O \cdot P_2O_5 \cdot 22\,WO_3 \cdot aq.$ by treatment with HCl. In addition to the desired compound, the potassium salt of 12-tungstic-1-phosphoric acid, $3\,K_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot aq.$, is also formed.

A conc. solution of $7\,K_2O \cdot P_2O_5 \cdot 22\,WO_3 \cdot aq.$ is prepared at the boiling point, and dilute (about 7%) HCl is added dropwise until the solution becomes acidic. An insoluble white precipitate of $3\,K_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot aq.$ appears. This is filtered off, and the filtrate is treated with KCl powder to salt out the desired compound. The latter is recrystallized from H_2O containing two drops of HCl.

PROPERTIES:

Formula weight 5293.6. Relatively large, lustrous, hexagonal columns, partly intergrown. Readily soluble in H_2O. The aqueous solution is unstable on boiling, depositing a white precipitate.

REFERENCES:

F. Kehrmann, Z. anorg. Chem. 1, 436 (1892); P. Souchay, Ann. Chimie [12] 2, 204 (1947). Checked by the present authors.

18-Tungstic Acid-2-Phosphates

Based on molecular weight determinations, these compounds should be regarded as salts of an 18-tungstic-2-phosphoric acid $H_6[(PO_4)_2(W_3O_9)_6 \cdot aq.]$ [G. Jander and F. Exner, Z. phys. Chem. (A) 190, 195 (1942)].

BioPBOOKS

The Ammonium Salt $3(NH_4)_2O \cdot P_2O_5 \cdot 18\,WO_3 \cdot aq.$

A solution of $Na_2WO_4 \cdot aq.$ is boiled for a long time with a large excess of phosphoric acid. This involves an apparently slow condensation reaction. The resulting solution of the sodium salt of 18-tungstic-1-phosphoric acid is treated with solid NH_4Cl to salt out the ammonium salt.

One mole of $Na_2WO_4 \cdot 2\,H_2O$ is dissolved in hot H_2O and treated with four moles of phosphoric acid (in the form of a conc. solution, d 1.17) and about 100 ml. of additional H_2O. The yellow solution is boiled for 3–5 hours while stirring and replacing the water lost by evaporation; the boiling point is 108°C. To remove any reduction products which may have formed, a few drops of nitric acid are added at the end. As the solution cools, solid NH_4Cl is added until the desired ammonium salt $3\,(NH_4)_2O \cdot P_2O_5 \cdot 18\,WO_3$ is completely precipitated and the solution becomes colorless. The salt is filtered out, redissolved in hot H_2O, and reprecipitated with conc. NH_4Cl solution. It is then filtered out again, washed and recrystallized twice from water; the first crystal fraction is discarded each time. An analytically pure preparation is thus obtained.

SYNONYM:

Ammonium luteophosphotungstate.

PROPERTIES:

Formula weight 4471.7. Lemon-yellow or pale yellow-green triclinic crystals. Water content: 14 moles of H_2O/mole. Soluble in H_2O.

REFERENCES:

F. Kehrmann. Z. anorg. Chem. 1, 432 (1892); Ber. dtsch. chem. Ges. 20, 1808 (1887); G. Jander and H. Banthien. Z. anorg. allg. Chem. 229, 142 (1936).

The Free Acid $P_2O_5 \cdot 18\,WO_3 \cdot aq.$

Obtained by the method of Drechsel (see p. 1700 f.) from the solution of the sodium salt described in the previous preparation.

It can also be prepared by ion exchange (cf. p. 1701), using a solution of 10 g. of $3\,(NH_4)_2O \cdot P_2O_5 \cdot 18\,WO_3 \cdot aq.$ in 50 ml. of H_2O. The eluate is clear and pale yellow-green. It is concentrated in a vacuum desiccator. Yield: 9 g.

SYNONYM:

Luteophosphotungstic acid.

PROPERTIES:

Formula weight 4315.4. M.p. 28°C. Lemon-yellow hexagonal tablets. Water content: 42 moles of H_2O/mole. Readily soluble in H_2O.

REFERENCES:

A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. 101, 261 (1917); G. Jander and F. Exner. Z. phys. Chem. (A) 190, 195 (1942); G. Jander and D. Ertel. Unpublished experiments.

12-Tungstic Acid-1-Arsenates

By analogy with the 12-tungstic acid-1-phosphates, compounds of this class should be regarded as salts of a 12-tungstic-1-arsenic acid $H_3[AsO_4(W_3O_9)_4 \cdot aq.]$ [J. W. Illingworth and J. F. Keggin, J. Chem. Soc. (London) 1935, 575].

All tungstic acid arsenates resemble closely the tungstic acid phosphates in their manner of preparation and their behavior. They are only a little less stable.

The Ammonium Salt $3(NH_4)_2O \cdot As_2O_5 \cdot 24\,WO_3 \cdot aq.$

Obtained by addition of NH_4Cl to a solution of the corresponding sodium salt $3\,Na_2O \cdot As_2O_5 \cdot 24\,WO_3 \cdot aq.$, which is not known to exist as a solid.

$$\underset{5981.9}{3\,Na_2O \cdot As_2O_5 \cdot 24\,WO_3\,(aq.)} + \underset{321.0}{6\,NH_4Cl} = \underset{5952.1}{3\,(NH_4)_2O \cdot As_2O_5 \cdot 24\,WO_3\,(aq.)} + \underset{350.7}{6\,NaCl}$$

A solution of 52.8 g. of $Na_2WO_4 \cdot 2\,H_2O$ is prepared by heating a mixture of the salt and sufficient water to make the final volume 90 ml. A second solution is prepared from 2.3 g. of As_2O_5 and 15 ml. of very concentrated aqueous NaOH, and is then diluted with water to a final volume of 70 ml. After cooling, both solutions are combined and treated with conc. HCl until the mixture is strongly acid (pH paper). This requires 15-20 ml. of conc. HCl. The resulting mixture is unstable; on long standing, a white sediment is formed. Therefore 21 g. of solid NH_4Cl is added immediately; the mixture is heated once to boiling and allowed to stand for two hours on a steam bath. The white precipitate is filtered out, washed first with NH_4Cl solution acidified with HCl and then with some cold H_2O, and dried in a desiccator.

PROPERTIES:

Fine white, crystalline precipitate. Water content: 12 moles of H_2O/mole. Relatively sparingly soluble in H_2O.

REFERENCES:

F. Kehrmann. Z. anorg. Chem. 22, 286 (1900); A. Rosenheim and J. Jaenicke. Z. anorg. allg. Chem. 101, 268 (1917). Checked by the present authors.

18-Tungstic Acid-2-Arsenates

These compounds are exactly the same in appearance and water content as the 18-tungstic acid-2-phosphates. The ammonium salt and the free acid are obtained by methods used for those compounds (see p. 1723), using arsenic acid instead of phosphoric.

Formula weights: $As_2O_5 \cdot 18\ WO_3 \cdot aq.$: 4404.4; $3\ (NH_4)_2O \cdot As_2O_5 \cdot 18\ WO_3 \cdot aq.$: 4560.6.

REFERENCES:

F. Kehrmann, Z. anorg. Chem. 22, 290 (1900); A. Rosenheim and J. Jaenicke, Z. anorg. allg. Chem. 101, 270 (1917).

6-Tungstic Acid-1-Tellurates

In keeping with their molecular weight, these compounds should be considered 6-tungstic acid-1-tellurates (salts of a 6-tungstic-1-telluric acid $H_8[TeO_6 \cdot 6\ WO_3 \cdot aq.]$) [G. Jander and K. F. Jahr, Kolloid-Beihefte 41, 308 (1935)].

The Guanidinium Salt $3(CN_3H_6)_2O \cdot TeO_3 \cdot 6\,WO_3 \cdot aq.$

Tungsten (VI) oxide is dissolved in guanidinium carbonate, HCl is added to ensure the level of acidity required for the formation of a heteropoly compound, and the required quantity of telluric acid is introduced.

$$\underset{1081.0}{6\,(CN_3H_6)_2CO_3} + \underset{229.6}{H_6TeO_6} + \underset{1391.5}{6\,WO_3} + \underset{218.8}{6\,HCl} = \underset{1975.6}{3\,(CN_3H_6)_2O \cdot TeO_3 \cdot 6\,WO_3\,(aq.)} + \underset{513.1}{6\,(CN_3H_6)Cl} + 6\,CO_2$$

A boiling aqueous solution of 0.06 moles of guanidinium carbonate is gradually treated (stirring) with 0.06 moles of fine yellow tungstic acid powder (not too strongly ignited). The tungstic acid dissolves. The solution is filtered, and 0.06 moles of HCl is added to the clear filtrate. The nascent precipitate is redissolved by addition of hot H_2O. Then, 0.01 moles of telluric acid is added. On cooling, the desired salt crystallizes out. It is recrystallized from hot H_2O.

PROPERTIES:

Pure white, well-formed platelike crystals. Relatively poor solubility in H_2O. Water content: 3 moles of H_2O/mole.

REFERENCE:

R. Haberle, Thesis, Univ. of Berlin, 1911.

Metatungstates, Dodecatungstates

In keeping with their molecular weight and structure, these compounds should be considered salts of a dodecatungstic acid $H_8[H_2O_4(W_3O_9)_4 \cdot aq.]$ [see, for example, G. Jander, Z. phys. Chem. (A) 187, 149 (1940); R. Signer and H. Gross, Helv. Chim. Acta 17, 1076 (1934); G. Schott and C. Harzdorf, Z. anorg. allg. Chem. 288, 15 (1956)]. P. Souchay [Ann. Chim. (11) 18, 1; 169 (1943)] terms the product obtained by acidification of a monotungstate a ψ-metatungstate. These compounds are hexatungstates, and also differ chemically from the "true" metatungstates, but they are not identical with the "paratungstates." [See G. Jander and U. Krüerke, Z. anorg. allg. Chem. 265, 244 (1951).]

The Sodium Salt $Na_2O \cdot 4WO_3 \cdot aq.$

I. $$\underset{3092.2}{5\,Na_2O \cdot 12\,WO_3\,(aq.)} + \underset{1854.9}{8\,WO_3} = 5\,[\underset{4947.1}{Na_2O \cdot 4\,WO_3\,(aq.)}]$$

A dilute solution of "sodium paratungstate" $5\,Na_2O \cdot 12\,WO_3 \cdot aq.$ is boiled with an excess of yellow tungstic acid hydrate until a filtered sample no longer gives a precipitate of tungstic acid when treated with dil. HCl. The solution is then filtered to remove the excess tungstic acid and the insoluble white products formed during boiling. The filtrate is concentrated somewhat on a steam bath and allowed to crystallize in a desiccator over H_2SO_4.

II. The salt may be prepared more simply as follows:

$$\underset{293.8}{Na_2WO_4\,(aq.)} + \underset{695.6}{3\,WO_3} = \underset{989.4}{Na_2O \cdot 4\,WO_3\,(aq.)}$$

A solution of 20 g. of $Na_2WO_4 \cdot 2\,H_2O$ in 200 ml. of H_2O is prepared and an excess of yellow tungstic acid is added to it in portions. The suspension is boiled for about 1.5 hours, which produces white insoluble precipitates, settling out together with the excess tungstic acid. The pH of the solution after boiling and filtration is about 3. It is concentrated as described above.

SYNONYM:

Sodium metatungstate.

PROPERTIES:

Colorless tetragonal bipyramids. Water content: 10 moles of H_2O/mole. The crystals effloresce easily, and lose almost all their water over H_2SO_4. Readily soluble in H_2O.

REFERENCES:

I. C. Scheibler. J. prakt. Chem. 83, 301 (1861).
II. Authors' experiments.

The Silver Salt $Ag_2O \cdot 4WO_3 \cdot aq.$

$$\underset{939.4}{Na_2O \cdot 4WO_3(aq.)} + \underset{339.8}{2AgNO_3} = \underset{1159.2}{Ag_2O \cdot 4WO_3(aq.)} + \underset{170.0}{2NaNO_3}$$

A solution of "sodium metatungstate" $Na_2O \cdot 4\ WO_3 \cdot aq.$ is allowed to react with a solution containing the equivalent quantity of $AgNO_3$. A white precipitate slowly crystallizes out.

PROPERTIES:

Small white scales. Water content: 3 moles of H_2O/mole. Quite insoluble in H_2O.

REFERENCE:

A. Rosenheim and F. Kohn. Z. anorg. Chem. 69, 250 (1911).

The Free Acid $H_2O \cdot 4WO_3 \cdot aq.$

The free acid may be isolated from a solution of $Na_2O \cdot 4\ WO_3 \cdot aq.$ (see above for preparation) by Drechsel's method (see p. 1700 f.). The oily ether addition product is best distributed onto several watch glasses, which are then placed in a fast stream of dry air. The product is then rapidly dried by pressing on clay plates. This affords a relatively stable preparation, which is soluble in H_2O, forming a clear solution. Some preparations convert to yellow tungstic acid in only a few days.

Better results are obtained if the acid is prepared by ion exchange (see p. 1701) from crystalline "sodium metatungstate." A solution of 20 g. of the sodium salt $Na_2O \cdot 4\ WO_3 \cdot aq.$ in 50 ml. of H_2O is used. The clear eluate does not hydrolyze when concentrated in a vacuum desiccator. White crystals. Yield: 18 g.

PROPERTIES:

Formula weight 945.5. Large octahedra; according to some authors, also rhombohedra or bipyramids; readily effloresce in air. Water content: 8 moles of H_2O/mole; some authors report deviation from this value. Readily soluble in H_2O. Dilute solutions may be kept in the cold for extended periods of time, but coagulation occurs on heating. Concentrated solutions often coagulate

even at moderately high temperatures. Because of its constitution and chemical behavior, this acid should be considered a heteropoly compound.

REFERENCES

A. Rosenheim and F. Kohn, Z. anorg. Chem. 69, 253 (1911); G. Jander and D. Ertel, Unpublished experiments.

12-Molybdic Acid-1-Silicates

In keeping with their constitution, all compounds of this composition are salts of a 12-molybdic-1-silicic acid $H_4[SiO_4(Mo_3O_8)_4 \cdot aq.]$ [J. W. Illingworth and J. F. Keggin, J. Chem. Soc. (London) 1935, 575].

The Sodium Salt $2Na_2O \cdot SiO_2 \cdot 12MoO_3 \cdot aq.$

The procedure given below affords a nitric acid-soluble solution of the sodium salt, which is the starting material for the preparation of the rubidium or cesium salts. Since this solution of the sodium salt also contains a very large quantity of $NaNO_3$, it cannot be used directly for the preparation of the crystalline sodium salt or the free acid (by Drechsel's method).

BiopBOOKS

$$\underset{2471.2}{12\,Na_2MoO_4\,(aq.)} + \underset{122.1}{Na_2SiO_3} + \underset{1386.4}{22\,HNO_3} = \underset{1911.5}{2\,Na_2O \cdot SiO_2 \cdot 12\,MoO_3\,(aq.)} + \underset{1870.0}{22\,NaNO_3}$$

Solid NaOH (60 g.) is dissolved in 400 ml. of boiling H_2O and a total of 172 g. of MoO_3 (free of ammonium salt) is added in portions during the course of 10–15 min. When this is completely dissolved, boiling is interrupted and 500 ml. of cold H_2O is poured in. Then 250 ml. of HNO_3 (d 1.39) is made up to 350 ml. with water, and portions of this are rapidly added to the molybdate with constant stirring. No appreciable amount of precipitate should form. The sodium silicate solution described below is added immediately in a thin stream and with constant stirring.

The sodium silicate solution is made by dissolving 28 g. of commercial crystalline $Na_2SiO_3 \cdot 9\,H_2O$ in 125 ml. of 2N NaOH and boiling 10–15 minutes to effect conversion to the monosilicate.

The solution of $2\,Na_2O \cdot SiO_2 \cdot 12\,MoO_3$ is intensely yellow and is not as stable as solutions of other heteropolysalts. It is therefore advisable to maintain the conditions specified above, particularly as far as the H^+ concentration is concerned.

A solution of the sodium salt is used in the potassium industry for recovering rubidium and cesium from carnallite.

Formula weight 1911.5.

REFERENCE:

G. Jander and F. Busch. Z. anorg. allg. Chem. 187, 173 (1930).

The Rubidium Salt $2Rb_2O \cdot SiO_2 \cdot 12MoO_3 \cdot aq.$

The Cesium Salt $2Cs_2O \cdot SiO_2 \cdot 12MoO_3 \cdot aq.$

$$\underset{1911.5}{2Na_2O \cdot SiO_2 \cdot 12MoO_3(aq.)} + \underset{483.8}{4RbCl}\ [\underset{673.5}{4CsCl}]$$
$$= \underset{2161.4}{2Rb_2O \cdot SiO_2 \cdot 12MoO_3(aq.)}\ [\underset{2351.1}{2Cs_2O \cdot SiO_2 \cdot 12MoO_3(aq.)}] + \underset{233.8}{4NaCl}$$

A nitric acid solution of the sodium salt described above is treated at about 65°C with a solution of RbCl or CsCl. Cooling to 40–50°C gives a fine yellow crystalline precipitate of the rubidium or cesium salt.

PROPERTIES:

Fine yellow powder. Relatively poor solubility in cold H_2O, better in hot.

REFERENCE:

G. Jander and H. Faber. Z. anorg. allg. Chem. 179, 323 (1929).

12-Molybdic Acid-1-Phosphates

In keeping with their structure, compounds of this class should be classified as salts of 12-molybdic-1-phosphoric acid $H_3[PO_4(Mo_3O_9)_4 \cdot aq.]$ [J. W. Illingworth and J. F. Keggin, J. Chem. Soc. (London) 1935, 575].

The Ammonium Salt $3(NH_4)_2O \cdot P_2O_5 \cdot 24MoO_3 \cdot aq.$

$$\underset{3975.6}{2[5(NH_4)_2O \cdot 12MoO_3(aq.)]} + \underset{284.0}{2Na_2HPO_4} + \underset{1134.4}{18HNO_3}$$
$$= \underset{3758.0}{3(NH_4)_2O \cdot P_2O_5 \cdot 24MoO_3(aq.)} + \underset{1120.7}{14NH_4NO_3} + \underset{340.0}{4NaNO_3}$$

A solution of 50 g. of Na_2HPO_4 in a mixture of 300 ml. of nitric acid (d 1.48) and 300 ml. of H_2O is prepared, cooled and

mixed with a clear, cold solution of 200 g. of commercial ammonium molybdate [this generally is $5\,(NH_4)_2O \cdot 12\,MoO_3 \cdot aq.$; see p. 1711] in the minimum of H_2O; the last solution is added in a thin stream and with stirring. A precipitate forms immediately. It is washed with hot H_2O to which a few drops of conc. HNO_3 have been added.

The ammonium salt is of value in analytical chemistry, where it is used for the determination and separation of phosphoric acid.

PROPERTIES:

Deep yellow, microcrystalline salt, soluble with great difficulty.

REFERENCE:

F. Kehrmann, Z. anorg. Chem. 7, 417 (1894).

The Free Acid $P_2O_5 \cdot 24MoO_3 \cdot aq.$

$$\underset{196.0}{2\,H_3PO_4} + \underset{3454.8}{24\,MoO_3} = \underset{3596.8}{P_2O_5 \cdot 24\,MoO_3\,(aq.)}$$

DropBooks

About 35 g. of MoO_3 is added in portions to a boiling solution of 6.3 g. of 25% phosphoric acid in 100 ml. of H_2O, and the boiling is continued for another 2-2.5 hours. The insolubles are removed by filtration and the yellow solution is shaken with ether to purify the crude product. It is unnecessary to add acid here. Further workup is the same as on p. 1701. Yield: about 20 g. The crystals thus obtained may be recrystallized from a small amount of hot water to which some HNO_3 has been added.

The success of the preparation depends on the availability of ammonium-free MoO_3. Commerical MoO_3 frequently contains some ammonium ions. To purify this material, the proper quantity is dissolved in an excess of pure aqueous NaOH and the solution is boiled until NH_3 can no longer be detected. The molybdic acid is reprecipitated by careful addition of conc. HNO_3. It is freed of HNO_3 and $NaNO_3$ by several decantantions with water and filtered out.

PROPERTIES:

Well-formed orange-yellow octahedra. Very readily soluble in H_2O. Water content: 63 moles of H_2O/mole. Melting range 78 to 98°C. Other hydrates also exist.

REFERENCE:

A. Rosenheim and J. Jaenicke, Z. anorg. allg. Chem. 101, 248 (1917). Checked by the present authors.

The Barium Salt $3BaO \cdot P_2O_5 \cdot 24MoO_3 \cdot aq.$

This salt is obtained by treatment of the free acid with $BaCl_2$ solution.

$$\underset{3596.8}{P_2O_5 \cdot 24\,MoO_3\,(aq.)} + \underset{624.9}{3\,BaCl_2} + \underset{54.0}{3\,H_2O} = \underset{4056.8}{3\,BaO \cdot P_2O_5 \cdot 24\,MoO_3\,(aq.)} + \underset{218.8}{6\,HCl}$$

A clear conc. solution of the free acid is mixed with excess hot, saturated $BaCl_2$ solution. The barium salt separates at once as coarse crystals. These are filtered out and washed with small amounts of cold H_2O, then recrystallized twice from hot H_2O to which some HNO_3 has been added.

PROPERTIES:

Lemon-yellow octahedra; appreciably soluble in H_2O.

REFERENCE:

F. Kehrmann, Z. anorg. Chem. 7, 417 (1894). Checked by the present authors.

18-Molybdic Acid-2-Phosphates

By analogy with the 18-tungstic acid-2-phosphates, compounds of this class should be classified as salts of an 18-molybdic-2-phosphoric acid $H_6[(PO_4)_2(Mo_3O_9)_6 \cdot aq.]$.

The Free Acid $P_2O_5 \cdot 18MoO_3 \cdot aq.$

The sodium salt of 18-molybdic-2-phosphoric acid is prepared first.

$$\underset{327.9}{2\,Na_3PO_4} + \underset{2591.1}{18\,MoO_3} = \underset{2919.0}{3\,Na_2O \cdot P_2O_5 \cdot 18\,MoO_3\,(aq.)}$$

The free acid is then obtained by Drechsel's method. Since the resulting product is still contaminated with 12-molybdic-1-phosphoric acid, the pure 12-molybdic-1-phosphoric acid is prepared by addition of H_3PO_4.

A boiling solution of Na_3PO_4 is treated with portions of MoO_3 (Na_3PO_4:MoO_3 mole ratio = 1:9). The solution is filtered and concentrated to a small volume. Any reduction products present are oxidized by means of some bromine water. The free acid is obtained from the solution by extraction with ether and HCl (see p. 1700 f.). The 18-molybdic-2-phosphoric acid thus prepared is never pure, but still contains rather large amounts of 12-molybdic-1-phosphoric acid. Therefore the aqueous solution of the acid is treated with sirupy phosphoric acid, the latter being added in a quantity corresponding to the amount missing in the formula. (Roughly, it may be assumed that about 1/3 of the heteropolyacid product is still in the form of 12-molybdic-1-phosphoric acid. To convert this, two moles of H_3PO_4 are required for three moles of $P_2O_5 \cdot 24\ MoO_3$ · aq.) The aqueous solution is allowed to stand until NH_4 or K salts cause no further precipitation. The free 18-molybdic-2-phosphoric acid then separates out in a vacuum desiccator over conc. H_2SO_4.

SYNONYM:

Luteophosphomolybdic acid.

PROPERTIES:

Formula weight 2733.06. Orange-colored prisms, readily soluble in H_2O. Several hydrates exist; various water contents are reported by individual authors. Quite unstable; an aqueous solution soon reverts to 12-molybdic-1-phosphoric acid.

DyeBooks

REFERENCE:

G. Jander and E. Drews. Z. phys. Chem. (A) 190, 228 (1942).

The Potassium Salt $3K_2O \cdot P_2O_5 \cdot 18MoO_3$ · aq.

May be obtained from a solution of the free acid by salting out with solid KCl.

A solution of 18-molybdic-2-phosphoric acid, as concentrated as possible, is treated in the cold with KCl powder until the desired potassium salt separates as a yellow precipitate.

PROPERTIES:

Formula weight 3015.64. Orange yellow, prismatic crystals. Water content: 14 moles of H_2O/mole. Soluble in H_2O.

REFERENCE:

F. Kehrmann. Z. anorg. Chem. 7, 147 (1894). Checked by the present authors.

12-Molybdic Acid-1-Arsenates

By analogy to the 12-molybdic acid-1-phosphates, which they very closely resemble, all compounds of this class should be classified as salts of a 12-molybdic-1-arsenic acid $H_3[AsO_4(Mo_3O_9)_4 \cdot aq.]$.

The Potassium Salt $3K_2O \cdot As_2O_5 \cdot 24MoO_3 \cdot aq.$

Commercial ammonium molybdate $5(NH_4)_2O \cdot 12\,MoO_3 \cdot aq.$ (see p. 1711) is heated with an excess of aqueous KOH, forming a solution of $K_2MoO_4 \cdot aq.$ Addition of HNO_3 and As_2O_5 yields the desired salt.

$$\underset{5715.4}{24\,K_2MoO_4(aq.)} + \underset{229.82}{As_2O_5} + \underset{2646.8}{42\,HNO_3} = \underset{3967.2}{3\,K_2O \cdot As_2O_5 \cdot 24\,MoO_3(aq.)} + \underset{4246.2}{42\,KNO_3}$$

Commercial ammonium molybdate (30 g.) is heated in a porcelain dish with an aqueous solution of KOH (one part of KOH by weight to two parts of H_2O) until all NH_3 has been driven off. (An excess of KOH should be avoided, since excessive quantities of KNO_3 are then formed during the reaction; this can crystallize out under some circumstances and contaminate the product.) After cooling, the solution is diluted with 50 ml. of H_2O and slowly poured into an excess of conc. HNO_3; external cooling may be used if required. The solution remains clear. It becomes deep yellow on addition of the stoichiometric quantity of As_2O_5 in 50 ml. of H_2O. It is briefly heated to 60–70°C to produce a yellow precipitate, more of which appears on cooling. Yield: about 8 g. about 8 g.

PROPERTIES:

Fine, yellow crystalline powder. Water content: 12 moles of H_2O/mole. Not particularly soluble in cold water, somewhat more soluble in hot.

REFERENCE:

O. Pufahl. Thesis, Univ. of Leipzig, 1888. Checked by the present authors.

18-Molybdic Acid-2-Arsenates

By analogy with the 18-molybdic acid-2-phosphates, these compounds should probably be classified as salts of an 18-molybdic-2-arsenic acid $H_6[(AsO_4)_2(Mo_3O_9)_6 \cdot aq.]$.

The Sodium Salt $3Na_2O \cdot As_2O_5 \cdot 18MoO_3 \cdot aq.$

Since the 18-molybdic acid-2-arsenates are more stable than the 12-molybdic acid-1-arsenates, $3\ Na_2O \cdot As_2O_5 \cdot 18\ MoO_3 \cdot aq.$ is produced when a sodium arsenate solution is treated with excess MoO_3.

$$\underset{415.8}{2\ Na_3AsO_4} + \underset{2591.1}{18\ MoO_3} = \underset{3006.9}{3\ Na_2O \cdot As_2O_5 \cdot 18\ MoO_3\ (aq.)}$$

A solution of Na_3AsO_4 is saturated with MoO_3 at the boil, and boiling is continued for some time. The deep-yellow solution is then filtered and concentrated. The desired sodium salt precipitates as yellow crystals.

PROPERTIES:

Yellow monoclinic crystals. Water content: 23 or 24 moles of H_2O/mole. Soluble in H_2O.

REFERENCE:

A. Rosenheim and A. Traube. Z. anorg. allg. Chem. 91, 92 (1915).

DropBooks

The Free Acid $As_2O_5 \cdot 18MoO_3 \cdot aq.$

I. Drechsel's method (see p. 1700) (that is, extraction of a solution of the sodium salt with HCl and ether) is used.

II. $$\underset{5351.6}{18\ BaMoO_4} + \underset{229.8}{As_2O_5} + \underset{1765.4}{18\ H_2SO_4} = \underset{2820.9}{As_2O_5 \cdot 18\ MoO_3\ (aq.)} + \underset{4201.6}{18\ BaSO_4}$$

Preparation of $BaMoO_4$: About 50 g. of commercial ammonium molybdate is dissolved in about 300 ml. of boiling H_2O (some ammonia is added). This solution is introduced gradually into a solution of 100 g. of $Ba(OH)_2 \cdot 8\ H_2O$ in 300 ml. of H_2O heated on a steam bath. The mixture is heated and stirred for 2-3 hours longer. The white precipitate is washed several times with hot H_2O, then heated once more with baryta water [aqueous $Ba(OH)_2$] and thoroughly washed.

The $BaMoO_4$ is suspended in a solution of arsenic acid so that one g.-atom of As is present per nine moles of MoO_3. Then the Ba is precipitated by addition of the stoichiometric quantity of H_2SO_4 (mechanical stirring). The filtered yellow solution is concentrated in vacuum at about 40°C and crystallized over conc. H_2SO_4.

PROPERTIES:

Deep-red triclinic crystals; decompose readily when stored damp. Water content: 28 moles of H_2O/mole. Quite soluble in H_2O. A yellow hydrate containing more water also exists.

REFERENCES:

A. Rosenheim and A. Traube. Z. anorg. allg. Chem 91, 91 (1915); O. Pufahl. Thesis, Univ. of Leipzig, 1888.

6-Molybdic Acid-2-Arsenates

According to molecular weight studies, the compounds of this class are salts of a 6-molybdic-2-arsenic acid $H_6[(AsO_4)_2(Mo_3O_9)_2 \cdot aq.]$ [G. Jander and E. Drews, Z. phys. Chem. (A) 190, 219 (1942)].

The Free Acid $As_2O_5 \cdot 6MoO_3 \cdot aq.$

$$\underset{1783.9}{6\,BaMoO_4} + \underset{229.8}{As_2O_5} + \underset{588.5}{6\,H_2SO_4} = \underset{1093.5}{As_2O_5 \cdot 6\,MoO_3\,(aq.)} + \underset{1400.5}{6\,BaSO_4}$$

A solution of 2.6 g. of As_2O_5 in 200 ml. of boiling H_2O is prepared; the hot solution is poured onto 20 g. of $BaMoO_4$ (one g.-atom of As per three moles of MoO_3). A solution of 6.6 g. of conc. H_2SO_4 in about 20 ml. of H_2O is added, and the mixture is heated for one hour on a steam bath (stirring). The $BaSO_4$ precipitate is filtered off, and the clear (sometimes greenish) solution is concentrated in a vacuum desiccator until crystallization.

PROPERTIES:

Large, fragile, colorless crystalline scales. Water content: 18 moles of H_2O/mole. Soluble in H_2O. The compound is a strongly held, very stable complex.

REFERENCE:

O. Pufahl. Thesis, Univ. of Leipzig, 1888. Checked by the present authors.

The Sodium Salt $Na_2O \cdot As_2O_5 \cdot 6MoO_3 \cdot aq.$

A solution of sodium paramolybdate $5\,Na_2O \cdot 12\,MoO_3 \cdot aq.$ is treated with the stoichiometric quantity of As_2O_5, and the salt

is synthesized by addition of HCl. However, only half of the theoretical quantity of HCl is used, since otherwise the salt decomposes.

A solution of "sodium paramolybdate" is prepared by dissolving three moles (431.9 g.) of MoO_3 in three moles (120.0 g.) of NaOH. One mole of H_3AsO_4 is added, and the clear solution is gradually treated with one mole of HCl. The desired salt crystallizes out on concentrating the solution.

PROPERTIES:

Formula weight 1155.5. Transparent, lustrous prisms. Water content: 12 moles of H_2O/mole. Readily soluble in H_2O.

REFERENCE:

A. Rosenheim and A. Traube. Z. anorg. allg. Chem. 91, 88 (1915).

12-Molybdic Acid-2-Chromites

The Ammonium Salt $3(NH_4)_2O \cdot Cr_2O_3 \cdot 12MoO_3 \cdot aq.$

$$\underset{1987.8}{5(NH_4)_2O \cdot 12MoO_3(aq.)} + \underset{586.5}{2KCr(SO_4)_2(aq.)} + \underset{18.0}{H_2O}$$
$$= \underset{2035.7}{3(NH_4)_2O \cdot Cr_2O_3 \cdot 12MoO_3(aq.)} + \underset{272.3}{2KHSO_4} + \underset{264.3}{2(NH_4)_2SO_4}$$

A solution of 2 g. of $KCr(SO_4)_2 \cdot 12\ H_2O$ in 20 ml. of H_2O is heated to boiling and a solution of 30 g. of ammonium paramolybdate $5\ (NH_4)_2O \cdot 12\ MoO_3 \cdot aq.$ in 110 ml. of H_2O is slowly added. During this operation the color of the solution changes from green to brownish and then bluish-rose. The pH of the solution should be about 5. On cooling, the desired rose-colored salt crystallizes out, although it sometimes takes 24 hours for this to occur. Yield: about 6 g.

PROPERTIES:

Relatively large, rose-colored rectangular platelets or scales. Water content: 20 moles of H_2O/mole. Quite soluble in hot H_2O, somewhat poorer solubility in cold H_2O. A relatively weak complex.

REFERENCE:

A. Rosenheim and H. Schwer. Z. anorg. allg. Chem. 89, 226 (1914).
Checked by the present authors.

DropBooks

6-Molybdic Acid-1-Periodates

These compounds are salts of a 6-molybdic-1-periodic acid $H_5[IO_6 \cdot 6\ MoO_3 \cdot aq.]$ [G. Jander and K. F. Jahr, Kolloid-Beihefte 41, 305 (1935)].

The Sodium Salt $5Na_2O \cdot I_2O_7 \cdot 12MoO_3 \cdot aq.$

$$\underset{543.9}{2\,Na_2H_3IO_6} + \underset{1727.4}{12\,MoO_3} + \underset{318.0}{3\,Na_2CO_3} = \underset{2393.6}{5\,Na_2O \cdot I_2O_7 \cdot 12\,MoO_3\,(aq.)} + 3\,CO_2$$

It has been found advisable to use two moles of Na_2CO_3 rather than the three moles called for by the equation.

A mixture of 10 parts by weight of $Na_2H_3IO_6$ and almost 32 parts of MoO_3 in about 120 parts of H_2O is heated. After a short time Na_2CO_3 (four parts) is added. When solution is complete, the liquid is concentrated to a small volume. Well-formed white, rhombohedral crystals appear, together with many-faceted, somewhat yellowish prisms.

PROPERTIES:

The rhombohedral crystals effloresce easily in air, becoming pure white and opaque. Water content: 34 moles of H_2O/mole. Readily soluble in H_2O.

The asymmetric, lustrous yellowish prisms do not effloresce in air. Water content: 26 moles of H_2O/mole. Soluble in H_2O.

The Free Acid $I_2O_7 \cdot 12MoO_3 \cdot aq.$

The free acid can be prepared by ion exchange (see p. 1701). Thus, 25 g. of $5\,Na_2O \cdot I_2O_7 \cdot 12\,MoO_3 \cdot aq.$ is dissolved in 100 ml. of H_2O. After passage through the column, the eluate is clear and colorless. Gas evolves during concentration in a vacuum desiccator. A bright-yellow crystalline compound is obtained. Yield: 22 g.

PROPERTIES:

Bright-yellow crystals; moderately soluble in cold H_2O, readily soluble in hot.

REFERENCES:

C. W. Blomstrand. Z. anorg. Chem. 1, 10 (1892); G. Jander and D. Ertel. Unpublished experiments.

48-Vanadic Acid-2-Phosphates and 24-Vanadic Acid-2-Phosphates

It was concluded from chemical and physicochemical studies that the anions of these heteropolyacid compounds consist of phosphate ions and ions of octavanadic acid $H_{10}(V_8O_{25} \cdot aq.)$ in varying molecular ratios [G. Jander and K. F. Jahr, Kolloid-Beihefte 41, 324 (1935)]. Other authors obtained compounds which they classify as salts of a 12-vanadic-1-phosphoric acid $H_7[PV_{12}O_{36} \cdot aq.]$ [A. Rosenheim and M. Pieck, Z. anorg. allg. Chem. 98, 223 (1916); P. Souchay and S. Dubois, Ann. Chimie (12) 3, 88 (1948)].

In addition to the compounds described here, there exists an immense number of salts of other compositions. The composition of the crystalline salt depends essentially on the molar ratio of phosphoric and vanadic acids in the starting solution, and also on the H^+ concentration, the nature of the cation, and the absolute concentration.

The brownish-red heteropolyacid compounds of this class, rich in vanadic acid, are designated in the older literature as "purpureophosphovanadates."

DropBooks

The Sodium Salt $10Na_2O \cdot P_2O_5 \cdot 24V_2O_5 \cdot aq.$

Prepared by combining solutions of $NaVO_3$, Na_2HPO_4 and HNO_3. Thus, the solution used is 0.75M in sodium metavanadate ($NaVO_3 \cdot aq.$), 0.315M in Na_2HPO_4, and 1.125M in HNO_3 (these quantities do not take the reaction into account); it therefore contains 2.38 moles of vanadic acid per mole of phosphoric acid. This deep-red solution is treated with 1/5 its volume of acetone and allowed to stand in the cold. After a while, the desired salt crystallizes out.

PROPERTIES:

Formula weight 5128.5. Small, dark-red octahedral crystals. Soluble in H_2O. Like all "purpureophosphovanadates," it is quite susceptible to hydrolysis; excessive heating of the solution must be avoided.

REFERENCE:

G. Jander and K. F. Jahr. Kolloid-Beihefte 41, 332 (1935).

The Barium Salt $10\,BaO \cdot P_2O_5 \cdot 24\,V_2O_5 \cdot aq.$

$$\underset{5185.5}{10\,Na_2O \cdot P_2O_5 \cdot 24\,V_2O_5\,(aq.)} + \underset{2613.8}{10\,Ba(NO_3)_2} = \underset{6041.2}{10\,BaO \cdot P_2O_5 \cdot 24\,V_2O_5\,(aq.)} + \underset{1700.2}{20\,NaNO_3}$$

A solution prepared in the same way as described for the sodium salt (50 ml.) is treated with 100 ml. of 0.375N $Ba(NO_3)_2$ solution and about 1/5 its volume of acetone. After standing for some time, the barium salt crystallizes out.

PROPERTIES:

Deep-red cubic crystals; poor solubility in H_2O.

REFERENCE:

G. Jander and K. F. Jahr. Kolloid-Beihefte 41, 332 (1935).

The Potassium Salt $11\,K_2O \cdot 2\,P_2O_5 \cdot 24\,V_2O_5 \cdot aq.$

The Ammonium Salt $5\,(NH_4)_2O \cdot 2\,P_2O_5 \cdot 24\,V_2O_5 \cdot aq.$

These are obtained from solutions of the sodium salt $10\,Na_2O \cdot P_2O_5 \cdot 24\,V_2O_5 \cdot aq.$ by means of KNO_3 or NH_4NO_3.

The same solution as described above in the case of the sodium salt (50 ml.) is treated with 100 ml. of 0.375N KNO_3 solution or 0.375N NH_4NO_3 solution and 1/5 its volume of acetone. After standing for some time, the desired salt crystallizes out.

PROPERTIES:

Formula weight of $11\,K_2O \cdot 2\,P_2O_5 \cdot 24\,V_2O_5$: 5685.5; formula weight of $5\,(NH_4)_2O \cdot 2\,P_2O_5 \cdot 24\,V_2O_5$: 4909.9. The potassium salt crystallizes in deep red rhombohedra, the ammonium salt in six-sided columns. Both are soluble in H_2O.

REFERENCE:

G. Jander and K. F. Jahr. Kolloid-Beihefte 41, 332 (1935).

SECTION 4

Carbonyl and Nitrosyl Compounds

F. SEEL

General Introduction

The classical method for the preparation of Mo, Fe, Co and Ni carbonyls consists of a direct reaction of CO with the respective metal at high pressures (150–200 atm.) and temperatures (100–200°C). Under these conditions steel is generally attacked by CO with formation of $Fe(CO)_5$, so that pressure vessels fully lined with a CO-resistant material (e.g., copper–silver alloy) must be used. Since such special autoclaves are not normally found in general-purpose chemical laboratories, this compilation of carbonyl syntheses will be restricted to preparative methods which are compatible with the usual laboratory apparatus, i.e., atmospheric-pressure syntheses or those requiring simple steel autoclaves.

With this goal in mind, several completely new methods were worked out [i.e., for $Ni(CO)_4$, $[Co(CO)_4]_2Hg$, $Co(CO)_3NO$], while in the case of others [$Fe(CO)_4H_2$, $Co(CO)_4H$] the apparatus used was improved. All methods were rechecked. For this we thank especially W. Hieber and his co-workers.

Descriptions of specific autoclaves for preparation of carbonyl compounds may be found in L. Mond, Z. anorg. Chem. 68, 207 (1910) and W. Hieber, H. Schulten and R. Martin, Z. anorg. allg. Chem. 240, 261 (1939).

Chromium, Molybdenum, Tungsten Carbonyls

$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$

The hexacarbonyls of the chromium group are formed via reaction of CO with a suspension of anhydrous halides of Cr, Mo or W in a Grignard solution, followed by hydrolysis. The reaction mechanism has not yet been elucidated.

The reactor vessel *f* in Fig. 343 is a one-liter flask fitted with a two-hole rubber stopper. The dropping funnel has a

considerably enlarged tip to prevent plugging during the reaction. R is used for the addition of the Grignard solution (via *a*), as well as that of CO (at *b*). Stopcock *h* is a gas vent which remains normally closed during the reaction but which is occasionally opened to allow flushing the reactor with CO. Flask *f* is fitted exactly into the ice bath *e*, and the whole apparatus is vigorously shaken on a machine. To monitor the CO consumption, a standardized gasometer is connected to *b* via a drying train (whose last tube is filled with P_2O_5).

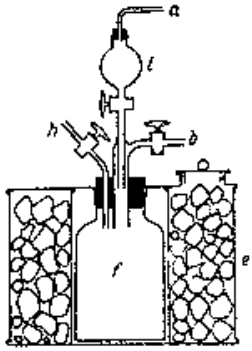

Fig. 343. Preparation of hexacarbonyls of the chromium group. *a* and *b* inlet tubes; *e* ice bath; *f* reactor vessel; *t* dropping funnel. Note that the tip of funnel *t* should be enlarged.

The reactor flask *f* is filled with nitrogen. The metal chloride (10 g. of fine anhydrous $CrCl_3$ powder; 17 g. of sublimed $MoCl_5$; or 20 g. of WCl_6 [0.05 moles]) is introduced, and the vessel is evacuated and filled with CO. A mixture of 50 ml. of anhydrous ether and 50 ml. of anhydrous benzene is added through the dropping funnel and the apparatus is then connected to the CO line.

The Grignard reagent is prepared from 12 g. (0.5 moles) of Mg, 54 g. of C_2H_5Br and approximately 300 ml. of anhydrous ether. This solution is added to the metal chloride suspension first in portions of about 5 ml. each, later dropwise. The initiation of the CO reaction as well as its progress may be observed via a wash bottle containing some conc. H_2SO_4 provided the stopcock of t is closed. The absorption of CO, which for reasons unknown occasionally slows down and then accelerates, is continued for about 4–6 hours after the addition of all of the Grignard reagent. The reaction absorbs on the average 7 liters and occasionally up to 9 liters of CO.

The reddish-brown reaction product is hydrolyzed by cautious addition to a mixture of ice and dilute H_2SO_4, and the mixture is then steam-distilled without prior removal of ether and benzene. The steam distillation is continued for 3–4 hours or as long as white needles of the carbonyl product are observed in the (descending) condenser. The organic layer (benzene-ether) in the distillate is separated and the aqueous phase extracted 3–4 times with fresh ether. The combined ether extracts are concentrated by distillation, keeping the temperature below 60°C, and the residue is allowed to crystallize in a refrigerator.

The yields of crude carbonyls are quite variable: in the case of $Cr(CO)_6$ they are 2 g. maximum, while up to 3–4 g. of $W(CO)_6$ may be isolated. Higher yields of $Cr(CO)_6$ (up to 67%) are obtained in an autoclave under high CO pressure (35–70 atm.). To remove strongly adhering, odorous organic impurities, an immediate vacuum sublimation of the hexacarbonyls is recommended.

PROPERTIES:

Formula weight of $Cr(CO)_6$: 220.1; of $Mo(CO)_6$: 264.0; of $W(CO)_6$: 352.0. Colorless, strongly refractive orthorhombic crystals which are isomorphic among themselves; well soluble in inert organic solvents and sublimable. $Cr(CO)_6$ melts at 149–50°C in a sealed tube. The hexacarbonyls are remarkably stable in comparison to all other metal carbonyls. Their vapors decompose above 120°C in a combustion tube, depositing the metals as mirrors.

DropBooks

REFERENCES:

W. Hieber and E. Romberg. Z. anorg. allg. Chem. 221, 321 (1935); B. B. Owen, J. English, Jr., H. C. Cassidy and A. V. Dundon. J. Amer. Chem. Soc. 69, 1723 (1947).

Iron Pentacarbonyl

$Fe(CO)_5$

Iron carbonyl is an industrial product which is prepared by classical carbonyl synthesis from CO and finely divided iron:

$$\underset{55.9}{Fe} + 5\,\underset{112.0\ l.}{CO} = \underset{195.9}{Fe(CO)_5}$$

This material serves as the starting substance for work in the field of iron carbonyls; laboratory preparation is not worthwhile since it requires the special autoclaves mentioned on page 1742.

There is, however, a method for the preparation of small quantities of $Fe(CO)_5$ in which a regular laboratory autoclave may be used; it starts with $Fe(CO)_4I_2$ (see p. 1751):

$$\underset{2108.5}{3\,Fe(CO)_4I_2} + \underset{636}{10\,Cu} \rightarrow \underset{}{10\,CuI} + \underset{783.6}{4\,Fe(CO)_5} + Fe$$

An intimate mixture of equal weights of $Fe(CO)_4I_2$ and copper dust is heated in a CO stream. The initial temperature is 40°C. It is then increased to 55°C and the $Fe(CO)_5$ (30% yield) is condensed in a U tube at −50°C.

If an autoclave at about 10 atm. pressure is used, the yield becomes nearly quantitative since the decomposition reaction

$$Fe(CO)_4I_2 = FeI_2 + 4\,CO$$

which occurs at atmospheric pressure, becomes impossible. Iron pentacarbonyl can then be distilled directly from the reaction vessel.

PROPERTIES:

At room temperature yellow, oily liquid, d^{20} 1.46. Vapor pressure equation in the range of 0 to 102.7°C.: $\log p = 7{,}349 - 1681/T$. At −25°C, solidifies to monoclinic needles; distills without decomposition at 102.6°C and 760 mm.; crit. temp. 285–288°C. Produces a metallic iron mirror on passage through a hot glass tube (200–350°C). Not altered in the dark; decomposed in light to $Fe_2(CO)_9$ and CO (must be stored in dark bottles). Pyrophoric in air (caution!); burns to Fe_2O_3. Nearly insoluble in water; readily soluble in many organic solvents, especially benzene, petroleum ether, ether, glacial acetic acid and acetone.

REFERENCE:

W. Hieber and H. Lagally. Z. anorg. allg. Chem. 245, 295 (1940).

Diiron Nonacarbonyl

$Fe_2(CO)_9$

Formed during decomposition of $Fe(CO)_5$ by light:

$$\underset{391.8}{2\,Fe(CO)_5} = \underset{363.8}{Fe_2(CO)_9} + \underset{22.4\ l.}{CO}$$

A solution of 20 g. of $Fe(CO)_5$ in 40 ml. of glacial acetic acid (or acetic anhydride) is prepared and exposed to direct sunlight

in an atmosphere of hydrogen or under vacuum. Very soon, turbidity and crystallization of $Fe_2(CO)_9$ are observed. The nascent CO is removed by flushing with H_2 or by reevacuation of the vessel. After several hours of illumination, the crystals are collected by filtration and washed with ethanol and ether. Minimum yield: 30% (5 g.). Further illumination of the mother liquors yields more $Fe_2(CO)_9$.

PROPERTIES:

Shiny, orange hexagonal platelets; d^{18} 2.085. Nearly insoluble in ether, petroleum ether and benzene; somewhat soluble in methanol, ethanol, and acetone; more readily soluble in pyridine. Stable at room temperature in dry air; on heating to 100–120°C, decomposes according to:

$$2\,Fe_2(CO)_9 = 2\,Fe(CO)_5 + 2\,Fe + 8\,CO$$

SYNONYM:

Diiron enneacarbonyl.

REFERENCE:

DropBooks

E. Speyer and H. Wolf. Ber. dtsch. chem. Ges. 60, 1424 (1927).

Triiron Dodecacarbonyl

$[Fe(CO)_4]_3$ or $Fe_3(CO)_{12}$

Oxidation of $Fe(CO)_4H_2$ gives $Fe(CO)_4$. The former may be prepared and oxidized in one consecutive process.

A) PREPARATION OF $Fe(CO)_4H_2$ SOLUTION:

$$\underset{195.9}{Fe(CO)_5} + 2\,\underset{80.0}{NaOH} = \underset{168.9}{Fe(CO)_4H_2} + \underset{106.0}{Na_2CO_3}$$

A two-liter flask is filled with N_2. Then, 14 ml. (= 20 g.) of $Fe(CO)_5$ and 60 ml. of methanol are added and agitated until a complete mixture of both liquids has been obtained. At this point, 30 ml. of 50% sodium hydroxide is added and, to avoid decomposition of the product, the mixture is cooled to 0°C. The reaction of the base with the pentacarbonyl occurs at room temperature and is completed after several minutes of shaking. Immediately after the addition of the base, the solution shows a milky turbidity due

to the formation of sodium methyl carbonate, which is only slightly soluble. Exposure to air (it is not necessary to exclude the latter completely to obtain the product) soon leads to a deep reddish-brown color.

B) OXIDATION WITH MnO_2

$$\underset{509.7}{3\,Fe(CO)_4H_2} + \underset{260.8}{3\,MnO_2} = \underset{503.7}{[Fe(CO)_4]_3} + \underset{212.8}{3\,MnO} + \underset{54.0}{3\,H_2O}$$

An aqueous suspension of MnO_2, prepared from 35 g. of $MnSO_4 \cdot 7\,H_2O$, 5.6 ml. of Br_2 and 20 g. of NaOH and purified by decantation, is added slowly with constant shaking to a freshly prepared solution of $Fe(CO)_4H_2$. The color of the reaction mixture changes immediately to a deep green. The excess MnO_2 is dissolved by addition of $FeSO_4$ in sulfuric acid or of $NaHSO_3$. At the end, 100 ml. of sulfuric acid (1 : 1) is added, resulting in a vigorous evolution of gas. After completion of the gas evolution, the solution is refluxed on a water bath for about 30 minutes. This coagulates the $Fe(CO)_4$; because it is hydrophobic, it floats on top of the solution as a dark green, crystalline mass. The product is collected on a fritted-glass filter, washed with hot, dilute H_2SO_4, H_2O, ethanol, and petroleum ether, and weighed in a desiccator. Yield: 90% (15–16 g.).

PROPERTIES:

Deep-green, nearly black, strongly dichroic square plates. Insoluble in water; slightly soluble (dark green color) in organic solvents such as benzene, petroleum ether, ether and acetone; more soluble in $Fe(CO)_5$ and $Ni(CO)_4$; in contrast to the other iron carbonyls, very sensitive to air. d^{18} 1.996; crystal structure: tetragonal.

REFERENCES:

W. Hieber, Z. anorg. allg. Chem. 204, 171 (1932); R. B. King and F. G. A. Stone in: Inorg. Syntheses, Vol. VII, New York-London, 1963, p. 193.

Cobalt Carbonyls

$[Co(CO)_4]_2$, $[Co(CO)_3]_4$

Decomposition of the hydride $Co(CO)_4H$ above its melting point gives $[Co(CO)_4]_2$:

$$\underset{344.0}{2\,Co(CO)_4H} = \underset{342.0}{[Co(CO)_4]_2} + \underset{22.4\,l.}{H_2}$$

The hydride $Co(CO)_4H$ (see p. 1753) is slowly evaporated under CO from a bath at an initial temperature of −30 °C, which

may be left unattended. Beautiful crystals of orange-red $[Co(CO)_4]_4$ remain as a residue.

Alternate method: Direct high-pressure synthesis from Co metal and CO [L. Mond, H. Hirtz and M. D. Cowap, Z. anorg. Chem. 68, 215 (1910)].

PROPERTIES:

Orange crystals, m.p. 51°C. Insoluble in H_2O; soluble in ethanol, ether and other organic solvents. Decomposes in air to the violet, basic Co carbonate. Melting of $Co(CO)_4$ results in a very slow decomposition to *cobalt tricarbonyl* $[Co(CO)_3]_4$; this reaction is clearly observable at 53°C and proceeds so fast at 60°C that it is complete after two days. After recrystallization from benzene, the tricarbonyl, formed according to the equation $Co(CO)_4 = Co(CO)_3 + CO$, consists of deep black crystals.

REFERENCE:

W. Hieber, F. Mühlbauer and E. A. Ehmann, Ber. dtsch. chem. Ges. 65, 1090 (1932).

DropBooks

Nickel Carbonyl

$Ni(CO)_4$

Forms even under such mild conditions as the reaction of CO with an alkaline solution of NiS. However, the reaction of CO with a solution of nickel sulfoxylate-ammonia complex, $NiSO_2 \cdot (NH_3)_x$, is especially recommended. This solution is easily prepared from $NiSO_4$, NH_3 and $Na_2S_2O_4$.

$$\underset{(\cdot 7\,H_2O)\ 280.9}{NiSO_4} + \underset{(\cdot 2\,H_2O)\ 210.2}{Na_2S_2O_4} + (x+2)\,NH_3 + H_2O = NiSO_2 \cdot (NH_3)_x + Na_2SO_4 + (NH_4)_2SO_3$$

$$NiSO_2 \cdot (NH_3)_x + H_2O + \underset{89.61.}{4\,CO} = \underset{170.7}{Ni(CO)_4} + (NH_4)_2SO_3 + (x-2)\,NH_3$$

The apparatus shown in Fig. 345 comprises a large gas-liquid mixing flask to which the shaking vessel shown in Fig. 344 can be attached. This mixing flask is attached to a large U tube filled with pea-sized calcium chloride granules and P_2O_5 deposited on glass beads. This tube is in turn attached to three condensing traps, two tees with stopcocks, and a bubble counter at the end of the train. The individual parts of the apparatus may be connected

by short pieces of rubber, provided glass touches glass; however, a ground-glass connection is required at *s* (this allows attaching the two condensing traps *k*, which are fused to each other, to a vacuum line).

The mixing flask is charged with a solution of 14.0 g. (0.05 moles) of $NiSO_4 \cdot 7\ H_2O$ in 400 ml. of water and 60 ml. of 25% aqueous ammonia. The carefully predried shaking vessel is charged with 12.5 g. of 80% $Na_2S_2O_4$; then 30 ml. of concentrated ammonia solution and 80 ml. of water are added under flowing nitrogen. The materials are dissolved by shaking, and the shaking vessel is attached to the mixing vessel by means of a rubber stopper, as shown in the figure. At this point CO, carefully prepurified to remove traces of iron carbonyl and oxygen, is passed through the clear blue nickel (II) salt solution; after a few minutes, a dropwise flow of the ammonial dithionite solution is started. (Pressures must be constantly equalized.) The dithionite solution is added over a period of about 20 minutes. The $Ni(CO)_4$ forms instantly and is condensed in the traps by cooling the latter with Dry Ice-acetone (or ethanol) mixture; the unreacted CO may be burned at t_2 after a reasonable flow rate has been established.

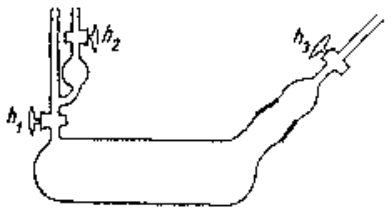

Fig. 344. Shaking vessel for work in the absence of air.

The nickel salt solution becomes nearly colorless in about 5 hours; a slight amount of decomposition, shown by the deposition of a mirrorlike layer of NiS_x on the glass walls, can not be avoided. Redistillation of the carbonyl (which condenses primarily in the first trap) in a stream of CO gives a completely pure product. Yield: 7.5 g. (5.5–6.0 ml.) of $Ni(CO)_4$ = 85–90%.

PROPERTIES:

Colorless liquid. M.p. −25°C, b.p. 43°C; d^{20} 1.310. Crit. temp. approximately 200°C, crit. pressure 30 atm. Insoluble in water, soluble in organic solvents. Readily oxidized in air;

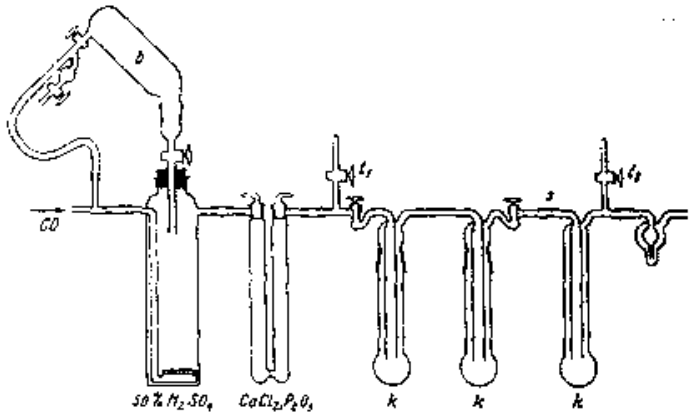

Fig. 345. Apparatus for the preparation of nickel carbonyl, carbonyl hydrides, and nitroyl carbonyls. *b* shaking vessel from Fig. 344; *k* condensing traps

burns with a luminous flame when ignited. A mixture with air is explosive. A bright Ni mirror is formed on passage through a heated tube at 180–200°C. The vapor is extraordinarily toxic.

DropBooks

REFERENCE:

W. Hieber, E. O. Fischer and E. Böckly. Z. anorg. allg. Chem., 269, 308 (1952).

Dipyridine Chromium Tetracarbonyl, Tripyridine Chromium Tricarbonyl

$Cr(CO)_4py_2$, $Cr(CO)_3py_3$

Up to one half of the CO contained in metal carbonyls can frequently be replaced by pyridine, o,o′-dipyridyl and phenanthroline.

$$\underset{220.1}{Cr(CO)_6} + \underset{156.2}{2\,py} = \underset{322.3}{Cr(CO)_4py_2} + \underset{44.8\,l.}{2\,CO}$$

$$\underset{220.1}{Cr(CO)_6} + \underset{237.3}{3\,py} = \underset{373.3}{Cr(CO)_3py_3} + \underset{67.2\,l.}{3\,CO}$$

A mixture of 1 g. of $Cr(CO)_6$ and 5 ml. of pure anhydrous pyridine is heated in a sealed tube for 2 hours at 200°C. [illegible] fraction of the $Cr(CO)_6$ separates unchanged on cooling [illegible]

deep-brown solution. The solution is filtered into a small distilling apparatus and most of the pyridine is quickly distilled off in a stream of N_2. On cooling the residue, crystals of $Cr(CO)_4py_2$ separate out; addition of petroleum ether increases the yield.

If 10-15 ml. of pyridine is used in the above experiment and the heating is repeated after discharge of the CO, the product is $Cr(CO)_3py_3$. Pyridine can be substituted into $Mo(CO)_6$ more readily than into $Cr(CO)_6$; the $Mo(CO)_6$ is converted into $Mo(CO)_3py_3$ on heating with pyridine for several hours at 135°C.

PROPERTIES:

$Cr(CO)_4py_2$: Blunt, yellowish-brown prisms. On heating, loses pyridine and turns brownish-black. $Cr(CO)_3py_3$: Yellowish-red to red prisms, stable in air; gives up pyridine very readily.

REFERENCE:

W. Hieber and F. Mühlbauer. Z. anorg. allg. Chem. 221, 341 (1935).

o-Phenanthroline Nickel Dicarbonyl

$Ni(CO)_2C_{12}H_8N_2$

$$\underset{170.7}{Ni(CO)_4} + \underset{180.2}{C_{12}H_8N_2} = \underset{294.9}{C_{12}H_8N_2 \cdot Ni(CO)_2} + \underset{44.8\,l.}{2\,CO}$$

Readily formed from solutions of equimolar quantities of the components in acetone or absolute ethanol. The almost immediate CO generation is preceded by a blood-red color of the reaction mixture. As the gas evolution increases, the compound separates in long needles (of the order of 1 cm.). After suction-filtration, the compound is washed with absolute ethanol, followed by petroleum ether.

PROPERTIES:

Ruby-red needles with high luster; very stable. Decomposed by air only in the presence of moisture (slow process, accompanied by a green color).

REFERENCE:

W. Hieber, F. Mühlbauer and E. A. Ehmann. Ber. dtsch. chem. Ges. 65, 1093 (1932).

Iron Tetracarbonyl Halides

$Fe(CO)_4X_2$

I. The simplest method consists of reacting the halogens with $Fe(CO)_5$ in organic solvents.

$$\underset{195.9}{Fe(CO)_5} + \underset{70.9}{Cl_2}, \underset{159.8}{Br_2}, \underset{253.8}{I_2} = \underset{248.8}{Fe(CO)_4Cl_2}, \underset{327.7}{Fe(CO)_4Br_2}, \underset{421.7}{Fe(CO)_4I_2} + \underset{22.4\,l.}{CO}$$

Pure $Fe(CO)_4Cl_2$ can be obtained only at −20°C by slow passage of Cl_2 through a 1M solution of $Fe(CO)_5$ in petroleum ether; the slight decomposition of the $Fe(CO)_5$ does not affect the purity of the product. The product (yield ~ 60%) is a yellow powder, which loses CO at room temperature and turns gray.

$Fe(CO)_4Br_2$ is prepared by slowly adding the reactants to a 2M petroleum ether solution, while cooling in ice and conducting the reaction under anhydrous conditions. The product is a reddish-brown powder. Yield: 75%.

$Fe(CO)_4I_2$ is obtained in anhydrous ether solution using a slight excess of $Fe(CO)_5$ [the ether solution is 2M in $Fe(CO)_5$ and 0.5M in I_2]. On evaporation, the compound separates in large, black crystals. Yield: quantitative.

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PROPERTIES:

The iron carbonyl halides are light-sensitive; water converts them to the corresponding Fe (II) salt solutions (the chloride and bromide react instantaneously, the iodide only upon heating). The thermal decomposition of iron carbonyl halides is a convenient way to produce fine powders of anhydrous Fe(II) halides.

II. $Fe(CO)_4I_2$ can be obtained from anhydrous FeI_2 and CO at pressures above 6.3 atm. Thus, it can be prepared in ordinary laboratory autoclaves.

$$\underset{309.7}{FeI_2} + \underset{89.6\,l.}{4\,CO} = \underset{421.7}{Fe(CO)_4I_2}$$

The preparation proceeds in anhydrous ethereal solution, using 50 ml. of ether/g. of FeI_2; the air is displaced from the autoclave by evacuating and flushing with CO (which may be taken directly from a cylinder). While the yield is quantitative, the duration of the CO absorption depends on the surface/volume ratio in the solution. Thus, in unagitated systems the reaction may occasionally take several days.

REFERENCES:

I. W. Hieber and G. Bader. Ber. dtsch. chem. Ges. 61, 1717 (1928); W. Hieber and H. Lagally. Z. anorg. allg. Chem. 245, 295 (1940); W. Hieber and A. Wirsching. Ibid. 245, 35 (1940).
II. W. Hieber and H. Lagally. Ibid. 245, 305 (1940).

Iron Tetracarbonyl Dihydride

$Fe(CO)_4H_2$

Solutions of alkali metal, alkaline earth metal, and ammonium salts of $Fe(CO)_4H_2$ may be produced by shaking solutions or suspensions of the corresponding hydroxides with $Fe(CO)_5$ in the absence of air. Addition of acid liberates the hydride.

$$\underset{195.9}{Fe(CO)_5} + \underset{120.0}{3\,NaOH} = \underset{191.9}{[Fe(CO)_4H]Na} + Na_2CO_3 + H_2O$$

$$\underset{191.9}{[Fe(CO)_4H]Na} + \underset{98.1}{H_2SO_4} = \underset{169.9}{Fe(CO)_4H_2} + NaHSO_4$$

The reaction may be conducted in the apparatus (Figs. 344 and 345) described for the preparation of $Ni(CO)_4$. After complete evacuation with an oil pump, the 200-ml. shaking vessel is charged with 7 ml. of $Fe(CO)_5$ (10 g., 0.1 moles), then with 25 g. of NaOH in 50 ml. of boiled water; the vessel walls are rinsed with some water and it is filled with oxygen-free nitrogen or CO. The reaction is complete after 5 hours of intensive mixing on a shaking machine. If no oxygen was present, a completely homogeneous, light-yellow solution of the sodium salt of $Fe(CO)_4H_2$ is produced. At this point, the mixing vessel is charged with 50 ml. of 50% sulfuric acid, the shaking vessel is attached, and the entire apparatus is flushed with oxygen-free CO (which can be ignited at t_2 after a reasonable flow rate has been attained).

The mixing vessel is then cooled to −10 to −15°C (ice-salt mixture) and the cold traps to −80°C (Dry Ice-acetone). The hydride solution from the shaking vessel is then decomposed by slow, dropwise addition to the mixing vessel. The liberated hydride is carried by the CO stream into the cold traps, where it condenses as a solid (if this fails to occur, the temperatures of the cooling baths are too high or the CO flow too high). Upon termination of the decomposition the apparatus is flushed with CO until a "carbonyl flame" is no longer visible on burning at t_2; this takes about one hour [see the section on $Ni(CO)_4$]. The hydride collected in the first two condensation traps is not yet

pure. It contains the products of its own decomposition, $Fe(CO)_5$ and $Fe(CO)_3$, and occasionally its oxidation product $Fe(CO)_4$. Repeated fractionation in high vacuum at −40°C, with condensation at −80°C, is necessary for complete purification. The removal of the last traces of $Fe(CO)_5$, which is frequently still present in small quantities (since it is re-formed during the distillation due to the extreme instability of the hydride), is achieved by repeated rapid distillation into a liquid-nitrogen-cooled vessel.

Since the isolation and purification of the free carbonyl hydride require considerable time, the acid decomposition should be started at the beginning of a full working day. $Fe(CO)_4H_2$ can be stored indefinitely, provided it is placed in suitable containers which are evacuated and cooled with liquid nitrogen.

PROPERTIES:

At the temperature of liquid nitrogen, a completely colorless, crystalline substance. M.p. −70°C. The autodecomposition

$$2\,Fe(CO)_4H_2 \rightarrow Fe(CO)_5 + Fe(CO)_3 + 2\,H_2$$

of the water-white, mobile liquid is already observed at −10°, as is indicated by a slight reddish color [$Fe(CO)_3$], but is completed only at higher temperature. The presence of even traces of $Fe(CO)_3$ and $Fe(CO)_5$ in the hydride is indicated by a weak red or yellow color; absence of color (only below −10°C) is a sensitive test for the purity of the product. The gaseous hydride has an extremely nauseating odor.

ErrorProducts

REFERENCES:

W. Hieber and H. Vetter, Z. anorg. allg. Chem. 212, 145 (1933).

An ether-soluble iron carbonyl hydride $Fe_4(CO)_{13}H_2$ was isolated from the reaction of pyridine-iron carbonyl with acids, [W. Hieber and R. Werner, Chem. Ber. 90, 286 (1957)].

Cobalt Tetracarbonyl Hydride

$Co(CO)_4H$

An alkaline suspension of $Co(OH)_2$ absorbs CO in the presence of a small amount of cyanide to form a solution of the alkali salt

of $Co(CO)_4H$. The hydride is then liberated from this solution with acid.

$$\underset{\substack{(+6\,H_2O)\\ 582.1}}{2\,Co(NO_3)_2} + \underset{246.4\,l.}{11\,CO} + \underset{673.2}{12\,KOH} = \underset{420.2}{2\,Co(CO)_4K} + 4\,KNO_3 + 3\,K_2CO_3 + 6\,H_2O$$

$$Co(CO)_4K + \underset{98.1}{H_2SO_4} = \underset{172.0}{Co(CO)_4H} + KHSO_4$$

The same apparatus as is shown in Figs. 344 and 345 (see preparation of $Ni(CO)_4$) is used. Since the acid decomposition of the alkaline hydride solution produces considerable foaming, a second mixing vessel, placed in series with the first one, is recommended. The evacuated shaking vessel is charged with 14.6 g. (0.05 moles) of $Co(NO_3)_2 \cdot 6\,H_2O$ in 30 ml. of water, 22.4 g. of KOH in 22 ml. of water, 10 ml. of water, 3.2 g. of KCN in 6 ml. of water (in this order), and finally with 10 ml. of water. Then stopcock h_1 is connected to a gas-liquid mixing vessel equipped with a fritted disk and containing an alkaline pyrogallol solution. The vessel is connected to a calibrated gasometer containing 6 liters of CO. After flushing the inlet piece via stopcock h_2, the gas is admitted to the shaking vessel; the latter is flushed briefly via h_3, h_3 is closed again, and the assembly is shaken on a machine under CO pressure. The CO absorption may be observed via the pyrogallol wash bottle: it varies with the intensity of shaking and even quantitative absorption may occasionally be achieved. During the absorption, the initially brown suspension is converted into a yellow solution which, in the case of absorption of the theoretical amount of CO, is nearly free of suspended matter and consists of a solution of $Co(CO)_4K$.

The free hydride is isolated in the same way as described in the preceding preparation of $Fe(CO)_4H_2$. On the same scale of preparation, the acid decomposition requires 50 ml. of 50% sulfuric acid. The hydride is finally sublimed from a bath maintained at −30°C to a cooler condensing trap.

PROPERTIES:

The pure solid hydride is completely colorless and crystalline; it melts at −26.2°C to a light-yellow solution which changes to dark yellow at slightly higher temperature (beginning of decomposition to $[Co(CO)_4]_2$). In gas form $Co(CO)_4H$ has a nauseating odor and is extremely toxic.

REFERENCES:

W. Hieber and H. Schulten. Z. anorg. allg. Chem. 232, 29 (1937); A. A. Blanchard and P. Gilmont. J. Amer. Chem. Soc. 62, 1192 (1940).

Iron Carbonyl Mercury

$Fe(CO)_4Hg$

$$\underset{195.9}{Fe(CO)_5} + \underset{296.7}{HgSO_4} + H_2O = \underset{388.5}{Fe(CO)_4Hg} + CO_2 + H_2SO_4$$

A solution of 7.5 g. (0.025 moles) of $HgSO_4$ in 50 ml. of 10% H_2SO_4 is shaken with 3.5 ml. (5 g.) of $Fe(CO)_5$ at room temperature to yield a dark-yellow, microcrystalline precipitate of $Fe(CO)_4Hg$. The precipitate is collected by filtration, washed several times with dilute H_2SO_4, 2-3 times with 2N HCl, then with water and acetone, and dried in vacuum.

PROPERTIES:

Insoluble in common solvents. Decomposes at about 150°C into Fe, Hg and CO. Reaction of $HgCl_2$ with $Fe(CO)_5$ gives $Fe(CO)_4Hg_2Cl_2$.

DropBooks

REFERENCE:

H. Hock and H. Stuhlmann. Ber. dtsch. chem. Ges. 61, 2097 (1928); 62, 431 (1929).

Cobalt Carbonyl Mercury

$[Co(CO)_4]_2Hg$

Produced by reaction of solutions of a salt of $Co(CO)_4H$ with Hg (II) salts. The optimum preparative method requires work in an ammonia solution.

$$\underset{378.0}{2\,[Co(CO)_4]NH_4} + \underset{271.5}{HgCl_2} = \underset{542.8}{[Co(CO)_4]_2Hg} + 2\,NH_4Cl$$

The potassium salt of $Co(CO)_4H$ is prepared as described on page 1754. However, only one half the amount is needed. The shaking vessel is evacuated, and 25 ml. of a saturated NH_4Cl

solution (corresponding to about 10 g. of NH_4Cl) and 3.5 g. of $HgCl_2$ in 100 ml. of water are added in that order. The instantly formed ochre precipitate consists of $[Co(CO)_4]_2Hg$, $HgNH_2Cl$ and traces of Hg. The reaction flask is immediately opened; the precipitate is collected by filtration (without any special protective measures) and washed twice with water, dilute hydrochloric acid (to dissolve $HgNH_2Cl$) and finally again with water. The crude product is dried in a desiccator and dissolved in some acetone; water is added until persistent turbidity. The product is left in a refrigerator to crystallize.

Alternate method: Precipitation from a solution of $[Co(CO)_4]NH_4$, as prepared by the dithionite method [see section on $Ni(CO)_4$, p. 1747 f.] [W. Hieber, E. O. Fischer and E. Böcky, Z. anorg. alleg. Chem. 269, 308 (1952)].

PROPERTIES:

Orange needles; very stable; insoluble in water and dilute nonoxidizing acids; readily soluble in ethanol, ether, acetone, benzene and other similar solvents [in contrast to $Fe(CO)_4Hg$]. An easily prepared compound and an excellent starting material for the preparation of other cobalt carbonyl compounds. Thus, $[Co(CO)_4]_2Hg$ may be converted by alkali sulfides into alkali salts of $Co(CO)_4H$, from which the hydride itself and $Co(CO)_4$ may be obtained.

In a similar manner, other heavy metal derivatives of $Fe(CO)_4H$ and $Co(CO)_4H$ may be obtained by this double decomposition. Derivatives of $Co(CO)_4H$ and Zn, Cd, Hg, In, Tl are obtained directly from the metals and CO in high-pressure syntheses.

REFERENCES:

W. Hieber and H. Schulten. Z. anorg. allg. Chem. 232, 24 (1937); W. Hieber and E. Fack. Ibid. 236, 101 (1938); W. Hieber and U. Teller. Ibid. 249, 43 (1942).

Ethylenediamine Iron Carbonyl

$$[Fe\,en_3]\,[Fe_2(CO)_8]$$

This and the next compound are complex salts of polynuclear iron carbonyl hydrides.

$$\underset{587.7}{3\,Fe(CO)_5} + \underset{180.2}{3\,en} = \underset{571.8}{[Fe\,en_3]\,[Fe_2(CO)_8]} + \underset{156.8\,l.}{7\,CO}$$

This compound can be successfully prepared only under completely anhydrous conditions. The ethylenediamine (*not* ethylene-

diamine hydrate) and the solvent pyridine must be completely free of water. The presence of pyridine is essential to the reaction. The apparatus shown in Fig. 346, consisting of the reaction vessel *a*, fritted-glass filter attachment *g*, and dropping funnel and adapter *t*, is recommended.

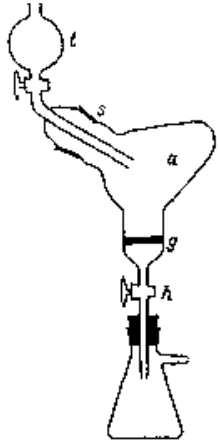

Fig. 346. Preparation of ethylenediamine iron carbonyl. *a* reaction vessel; *g* fritted-glass filter; *h* stopcock; *s* ground joint adapter; *t* dropping funnel attachment.

Dropsbooks

With vessel *a* pointed downward, a solution of 1.4 g. of the diamine in 20 ml. of pyridine is mixed with 8 g. of $Fe(CO)_5$; vessel *a* is closed with a ground-glass stopper at *s* and connected to the atmosphere via the stopcock *h* and a wash bottle filled with conc. H_2SO_4. The reaction mixture is then heated on a water bath to 80°C for four to five hours. After about one hour of heating the (now red) solution starts evolving gas bubbles and continues to do so until the reaction is finished. At end of the reaction, the solution is cooled, the dropping funnel *t* is connected to *s*, and the product, which forms in copious quantities, is filtered through *g*. It is washed on *g* with pyridine and anhydrous ether; for a final purification, it is again triturated with ether and refiltered. Yield: 2.6 g. (60% on the basis of the diamine).

SYNONYM:

Triethylenediamine iron (II) octacarbonyl diferrate (II).

PROPERTIES:

Brick-red monoclinic (or triclinic) and very shiny prisms; quite stable; insoluble in organic solvents, including pyridine.

REFERENCES:

W. Hieber and F. Sonnekalb. Ber. dtsch. chem. Ges. 61, 563 (1928); W. Hieber, J. Sedlmeier and R. Werner. Chem. Ber. 90, 278 (1957).

Pyridine Iron Carbonyl

$$[Fe\ py_4]\ [Fe_4(CO)_{13}]$$

$$\underset{839.4}{5\,Fe(CO)_4} + \underset{474.6}{6\,py} = \underset{1117.9}{[Fe\ py_4]\ [Fe_4(CO)_{13}]} + \underset{156.8\,l.}{7\,CO}$$

This substance must be prepared in complete absence of air and under nitrogen; this is best done in the apparatus shown in Fig. 346.

The bulb is charged with 5 g. of $Fe(CO)_4$; the latter is then freed of the always present traces of Fe_3O_4. This is done by pouring over it some methanol and then heating with 20% HCl on a water bath for four to six hours (no oxygen may be present). The solution is suction-filtered through the fritted glass and washed with dilute HCl, dry methanol and dry ether; the residue is dried in a high vacuum. For this final drying, the dropping funnel is replaced by a stopper at *s* and the apparatus connected at *k* to a cooled trap and the vacuum pump.

The purified $Fe(CO)_4$ is then reacted at 0°C with 6 ml. of dry and air-free pyridine, the reaction taking place in the evacuated apparatus. The reaction is accompanied by foaming and evolution of CO, and ends in a short while, the green color of the $Fe(CO)_4$ solution turning intense red.

After 0.5 hour the product is collected by filtration, washed briefly with pyridine, then with dry petroleum ether and absolute ether, and dried in a high vacuum. Yield: 2.3 g. (70%), the remainder being retained in the mother liquor.

Alternate method: Direct synthesis from $Fe(CO)_5$ and pyridine in a sealed tube at 120–140°C.

SYNONYM:

Hexapyridine iron (II) tridecacarbonyl tetraferrate (II).

PROPERTIES:

Nearly black or deep-red crystals, extremely pyrophoric.

REFERENCES:

W. Hieber and E. Becker. Ber. dtsch. chem. Ges. 63, 1414 (1930); W. Hieber and F. Mühlbauer. Ibid. 65, 1088 (1932); W. Hieber and R. Werner. Chem. Ber. 90, 286 (1957).

Potassium Nitrosyl Tricarbonyl Ferrate

$[Fe(CO)_3NO]K$

$$\underset{195.9}{Fe(CO)_5} + \underset{85.1}{KNO_2} = \underset{209.0}{[Fe(CO)_3NO]K} + CO + CO_2$$

The reactor in this case is a one-liter, three-neck flask fitted with stirrer, reflux condenser and gas inlet tube. To start with, the air is completely displaced with very pure nitrogen; then, 45 g. of KNO_2 is dissolved in 400 ml. of methanol with vigorous stirring (the KNO_2 is premelted and then cooled on a cold porcelain surface to give small droplets). Following this, 67 ml. (0.5 moles) of freshly distilled $Fe(CO)_5$ is added via the condenser and the mixture is cautiously heated to 30–35°C. The reaction starts in a short while and is accompanied by vigorous evolution of gas; since the reaction is highly exothermic, it must occasionally be moderated by cooling in cold water. The gas evolution slows down in about three hours; the mixture is heated at 60°C for 30 minutes and then cooled. Finally, the stirrer and the reflux condenser are replaced by stoppers, and the solvent and unreacted carbonyl compound are distilled off in aspirator vacuum. To shorten this distillation somewhat, it is permissible to heat slightly (but very carefully).

The dry crude product can be used immediately for the preparation of $Fe(NO_2)(CO)_2$. However, there may arise a need to purify it, especially to remove excess nitrite and decomposition products. In this case, the crude product is extracted (in the absence of air and light) in a Soxhlet apparatus with 200 ml. of ether until the reflux is colorless. Evaporation of the extract under reduced pressure yields a bright-orange mass. Addition of toluene or xylene to the ether solution gives the salt as fine crystals. Yield: 60 g. of crude product, which on careful workup yields 45 g. of pure substance.

DropBooks

PROPERTIES:

Orange-yellow salt, very sensitive to light and air, especially when in solution. All operations, including the purification, should be conducted in a darkroom under red light. The product is kept in a vacuum desiccator lined with black paper; the desiccator is preflushed several times with nitrogen, and is then evacuated. When stored under such conditions, the preparation is stable for some time.

The sodium salt is obtained in nearly quantitative yield by reaction of $Fe(CO)_5$ with $NaNO_2$ in absolute methanol in the presence of 2 molar equivalents of $NaOCH_3$ per mole of $Fe(CO)_5$.

REFERENCES:

W. Hieber and H. Beutner, Z. Naturforschg. 15b, 323 (1960); M. J. Hogsed, C.A. 53, 9592 (1959), U. S. Pat. 2,865,707 (1957).

Iron Dinitrosyl Dicarbonyl

$Fe(NO)_2(CO)_2$

$$\underset{83.1}{KNO_2} + \underset{209.0}{[Fe(CO)_3NO]K} + CO_2 + H_2O \rightarrow \underset{171.9}{Fe(CO)_2(NO)_2} + 2\,KHCO_3$$

This compound is prepared in the same apparatus as nickel carbonyl (p. 1747 ff.; Figs. 344 and 345). First, the shaking vessel, which in this case is used as a dropping funnel, is charged with 42 g. (0.2 moles) of $[Fe(CO)_3NO]K$; after evacuation, a solution of 17 g. of KNO_2 or 14 g. of $NaNO_2$ in 150 ml. of water is added. Then, the shaking bulb is attached to the gas-liquid mixing vessel and the entire apparatus flushed with a moderately fast stream of air-free CO_2.

The brown nitrosyl carbonyl vapor appears the moment the solution is allowed to flow into the mixing vessel; the vapor is condensed in the Dry Ice-cooled traps, where it deposits as a bright orange coating. To speed up the transfer of the vapor to the traps, the reaction flask is heated in a water bath. However, the flask temperature should not exceed 35°C. If, as may happen (especially at the start of the experiment), some of the vapor condenses in the connecting tubes, it is driven into the cold traps by gentle heating with a hair dryer. The brown vapor disappears after a while, the preparation is stopped, and the CO_2 in the apparatus is displaced with pure nitrogen. The produce may be resublimed onto P_2O_5 in high vacuum; from there, it may be driven into ampoules, which are then stored in a freezer and protected from light to avoid decomposition. The yield is approximately 20–25 g. (60–70%).

PROPERTIES:

Beautiful deep-red crystals. M.p. 18.5°C. The liquid has a tendency to supercool; decomposes at 50°C. Insoluble in water, soluble in organic solvents; readily oxidized by air. Can be distilled without extensive decomposition only at temperatures below 15°C.

REFERENCES:

W. Hieber and J. St. Anderson, Z. anorg. allg. Chem. 208, 238 (1932); 221, 132 (1933); F. Seel, Ibid. 269, 40 (1952).

Cobalt Nitrosyl Tricarbonyl

$Co(NO)(CO)_3$

Prepared in the same way as $Fe(NO)_2(CO)_2$, that is, by reaction of the solution of $Co(CO)_4K$ obtained in the cyanide process with nitrite and CO_2.

$$\underset{210.1}{[Co(CO)_4]K} + \underset{85.1}{KNO_2} + 2\,CO_2 + 2\,H_2O = \underset{171.0}{CO(NO)(CO)_3} + 2\,KHCO_3$$

PROPERTIES:

Cherry-red, very volatile liquid; m.p. −1.05°C, b.p. 48.6°C, decomposition temperature 55°C. Insoluble in water and very stable if kept under water; miscible in all proportions with ethanol, ether, acetone, benzene and other organic solvents.

REFERENCES:

W. Hieber and J. St. Anderson. Z. anorg. allg. Chem. 208, 238 (1932); 221, 132 (1933); F. Seel. Ibid. 269, 40 (1952).

DropBooks

Dinitrosyl Cobalt Halides

$(NO)_2CoCl$, $(NO)_2CoBr$, $(NO)_2CoI$

$$\underset{259.8}{2\,CoCl_2} + \underset{65.4}{Zn} + \underset{89.6\,l.}{4\,NO} = \underset{364.8}{2\,(NO)_2CoCl} + ZnCl_2$$

$$\underset{437.6}{2\,CoBr_2} + Zn + 4\,NO = \underset{453.8}{2\,(NO)_2CoBr} + ZnBr_2$$

$$\underset{625.6}{2\,CoI_2} + 4\,NO = \underset{547.6}{2\,(NO)_2CoI} + I_2$$

The apparatus consists of a 70-cm.-long, 2-cm.-O.D. glass tube surrounded by a 15-cm.-long metal block with a thermometer well. The block is heated with a gas burner, the temperature being controlled automatically by means of a relay-actuated valve in the gas line, which in turn is tripped by a bimetallic element in the thermowell. The reactor tube is connected to a tee so that either dry N_2 or NO_2 may be passed through. The NO is generated from $NaNO_2$ and 20% H_2SO_4, washed free of NO_2 with 50% KOH, and dried in a train consisting of flask filled with conc. H_2SO_4, $CaCl_2$, NaOH and P_2O_5 (in that order). All parts

of the apparatus are either connected with ground joints or fused together.

The raw material for the iodine compound consists of about 2 g. of anhydrous CoI_2 placed in a porcelain boat, which is then inserted into the front part of the glass tube; the latter is then closed off with a wash bottle containing conc. H_2SO_4. The traces of moisture carried in with the CoI_2 are then removed by heating to 130°C (by means of the metal block) while passing through a stream of N_2. After cooling, the N_2 is displaced with NO and the temperature is again raised to 70-80°C. At this point, the reaction of NO with CoI_2 is so rapid that the pressure in the apparatus drops to below atmospheric; at the same time copious amounts of iodine are given off. The substance sinters and takes on a violet sheen. The temperature is now raised to 105°C and maintained at that level for 15-20 hours, that is, until the iodine vapors are displaced by brown vapors of the nascent $(NO)_2CoI$. The final residue in the porcelain boat is a viscous, blackish-brown mass.

The product must be sublimed. Thus, the boat is transferred, in a countercurrent stream of N_2, to the other end of the reactor tube and the temperature is raised to 115°C. The beginning of the sublimation is noticeable by a brown deposit; at a later stage, beautiful, flexible, deep brown-black, glittering crystals, up to 15 mm. long, are formed.

The chlorine and bromine compounds are prepared in the same way, except that a halogen-trapping metal (such as Zn dust or Co powder) must be added in 20% excess.

PROPERTIES:

Formula weight of $(NO)_2CoCl$: 182.4; $(NO)_2Br$: 226.9; $(NO)_2CoI$: 273.9. After sublimation, these compounds form beautiful black-brown needles with a diamondlike glitter; these are often 1 cm. long. Melting points: $(NO)_2CoCl$: 101°C; $(NO)_2CoBr$: 116°C; $(NO)_2CoI$: 131°C. The freshly prepared compounds are stable for some time in air; however, the crystals lose their surface sheen in several hours and then decompose over a period of days with loss of NO. The solubility in water increases in the sequence I-Br-Cl (partial decomposition).

In an analogous fashion iron (II) halides yields the dinitrosyl iron halides, $(NO)_2FeX$, upon which Roussin's salts are based.

REFERENCES:

W. Hieber and R. Marin. Z. anorg. allg. Chem. 240, 241 (1939); W. Hieber and R. Nast. Ibid. 244, 23 (1940).

Sodium Dinitrosyl Thioferrate*

$$Na[(NO)_2FeS] \cdot 4\,H_2O$$

$$\underset{(\cdot H_2O)}{2\,(NH_4)[(NO)_2Fe_4S_3]} + 6\,NaOH$$

(1/10): 113.1 24.0

$$= \underset{(\cdot 4\,H_2O)}{6\,Na[(NO)_2FeS]} + 2\,Fe(OH)_3 + N_2O + 2\,NH_3 + H_2O$$

145.8

A mixture of 10 ml. of 10% NaOH with 3 g. of Roussin's black ammonium salt is prepared and heated on the water bath at 80°C; the heating is continued until the ammonia odor disappears (in about 15 minutes). The $Fe(OH)_3$ precipitate is removed by suction filtration through a fritted-glass funnel and the reddish-brown solution is evaporated over $CaCl_2$ under reduced pressure. It is left standing for one day; beautiful black-red crystals separate. These are collected on a fritted-glass funnel, washed with 0.1% sodium hydroxide solution, and dried between filter papers.

DropBooks

SYNONYM:

Roussin's red sodium salt.

PROPERTIES:

Formula weight of $Na[(NO)_2FeS]$ 170.92; of $Na[(NO)_2FeS] \cdot 4\,H_2O$ 242.99. Reddish-black crystals or reddish-brown powder, soluble in water and ethanol; insoluble in ether. Upon removal of excess base, the compound is converted in a short time to the black Roussin's salt.

REFERENCES:

O. Pawel. Ber. dtsch. chem. Ges. 12, 1953 (1879); 15, 2607 (1882).

*The nomenclature used here and in the following preparations is justified by the nature of these complex salts, in which the NO group is bound in the same way as in the nitrosyl carbonyls. See F. Seel, Z. anorg. allg. Chem. 249, 308 (1942).

Ammonium Heptanitrosyl Trithiotetraferrate

$$NH_4[(NO)_7Fe_4S_3] \cdot H_2O$$

$$52\,FeSO_4 \cdot 7\,H_2O + 42\,NaNO_2 + 34\,(NH_4)_2S \quad (68\,NH_3 + 34\,H_2S) + 42\,H_2O$$

(·7 H_2O) (M_{mol}: 144.6) 29.0 11.6 7.6 l.

$$= 6\,NH_4[(NO)_7Fe_4S_3] + 28\,Fe(OH)_3 + 16\,S + 21\,Na_2SO_4 + 31\,(NH_4)_2SO_4$$

(·H_2O) 33.9 29.9 5.1

A solution of 8 g. of $NaNO_2$* in 40 ml. of water is mixed with a solution of $(NH_4)_2S$, prepared by saturating 5 ml. of 22% ammonium hydroxide with H_2S adding 5 ml. of ammonium hydroxide of the same concentration, and diluting with 30 ml. of water. The final mixture is heated to the boil and thus becomes a dark-brown. Now, a solution of 20 g. of $FeSO_4 \cdot 7\,H_2O$ in 160 ml. of water is added at once and the mixture is quickly reheated to a vigorous boil. The reaction starts even before the boiling point is reached [precipitation of $Fe(OH)_3$ and S is evident from the color change to black and brown]. Almost simultaneously the mixture starts evolving nitrous fumes. If a good yield is desired, it is essential that the gas evolution be suppressed by addition of 25 ml. of ammonium hydroxide (in small portions) during the entire boiling operation. After boiling for 15 minutes, the hot solution is filtered as quickly as possible through two Buchner funnels (moderate vacuum). The small crystals of Roussin's black ammonium slat already begin to precipitate in the filtrate during the filtration. To obtain larger crystals, the filtrate is placed in a hot water bath, heated until the salt is completely dissolved, and allowed to cool in the bath. Yield: about 1.7 g.

SYNONYM:

Roussin's black ammonium salt.

PROPERTIES:

Formula weight of $NH_4[(NO)_7Fe_4S_3] \cdot H_2O$: 565.7. Hard, monoclinic crystals with a diamondlike glitter; soluble in water, giving dark-brown solutions; stable to 80°C.

The corresponding alkali salts are obtained by a similar procedure; however no excess of nitrite is necessary in this case.

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*This is about double the theoretical amount; this compensates for the decomposition of the NH_4NO_2 present in the solution.

REFERENCES:

O. Pawel. Ber. dtsch. chem. Ges. 12, 1953 (1879); 15, 2607 (1882).

Ethyl Dinitrosyl Thioferrate

$[(NO)_2Fe\,SC_2H_5]_2$

$$\underset{(\cdot 7\,H_2O)}{2\,FeSO_4} + \underset{224.4}{4\,KOH} + \underset{62.1}{C_2H_5SH} + \underset{44.8\,l.}{2\,NO} = \underset{177.0}{(NO)_2FeSC_2H_5} + Fe(OH)_3 + K_2SO_4 + H_2O$$

The shaking vessel shown in Fig. 344 is charged with 27.8 g. (0.1 moles) of $FeSO_4 \cdot 7\,H_2O$ and evacuated. Then, 140 ml. of boiled water is aspirated in, the salt is dissolved by shaking, and finally a solution of 11.2 g. of KOH and 3.1 g. of C_2H_5SH (3.7 ml., 0.05 moles) in 25 ml. of water is added. The apparatus is now connected to a calibrated gas-measuring flask containing 2.5 liters of NO stored over some solid KOH; the gasometer is then shaken on a machine. The initially sirupy, off-color slurry of $Fe(OH)_2$ and $Fe(SC_2H_5)_2$ becomes a deep olive-green liquid. Toward the very end of the NO absorption (which goes very fast at the beginning and takes about 1.5 hours), the color changes to a light brown. A small amount of deep-black crystals are evident at the bottom of the flask and sometimes at the surface of the liquid. The NO is displaced with N_2 and the flask is opened. The black crystals can be separated from the $Fe(OH)_3$, which has a lower specific gravity, by decantation and slurrying; however, better yields (up to 80%) are obtained by centrifugation, washing in the centrifuge tube (once with absolute ethanol and 3-4 times with ether), and recrystallization of the substance from hot absolute ethanol with slow cooling.

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PROPERTIES:

Glittering black monoclinic crystals, m.p. 78°C. Insoluble in water; soluble with difficulty in ethanol; more readily soluble in ether; readily soluble in CS_2, $CHCl_3$ and C_6H_6, giving yellowish-red solutions.

REFERENCES:

K. A. Hofmann and O. F. Wiede. Z. anorg. Chem. 9, 300 (1895); H. Reihlen and A. von Friedolsheim. Liebigs Ann. 452, 71 (1927).

Potassium Dinitrosyl Thiosulfatoferrate

$$K[(NO)_2FeS_2O_3] \cdot H_2O$$

$$\underset{(\cdot 7\,H_2O)\ 556.0}{3\,FeSO_4} + \underset{761.2}{4\,K_2S_2O_3} + \underset{89.61.}{4\,NO} = \underset{(\cdot H_2O)\ 516.2}{2\,K[(NO)_2FeS_2O_3]} + K_2S_4O_6 + 2\,K_2SO_4$$

This derivative of Roussin's red salt is prepared by shaking a mixture of the concentrated aqueous solutions of 28 g. (0.1 moles) of $FeSO_4 \cdot 7\,H_2O$ and 40 g. of $K_2S_2O_3$ under NO, as described in the previous preparation. During the first hour, the gas is absorbed especially rapidly and the solution turns intensely brown. Later, $K[(NO)_2FeS_2O_3] \cdot H_2O$ separates out in leaflets of brass-like glitter. The substance is collected by filtration, washed with ethanol, and dried in vacuum over conc. sulfuric acid.

PROPERTIES:

Formula weight of $K[(NO)_2FeS_2O_3] \cdot H_2O$: 258.1. Only slightly soluble in cold and warm water; decomposes in boiling water.

The same procedure is used to prepare the sodium salt, $Na[(NO)_2FeS_2O_3]$. In this case, crystallization is slower due to the greater solubility of the product.

Finally, the same method may be used for the preparation of the corresponding cobalt and nickel compounds $K_3[(NO)_2Co(S_2O_3)_2]$, and $K_3[(NO)Ni(S_2O_3)_2]$.

REFERENCES:

K. A. Hofmann and O. F. Wiede. Z. anorg. Chem. 8, 319 (1895); W. Manchot. Ber. dtsch. chem. Ges. 59, 2445 (1926).

Potassium Nitrosyl Cyanomolybdate

$$K_4[(NO)Mo(CN)_5] \cdot H_2O$$

$$\underset{144.0}{MoO_3} + \underset{325.6}{5\,KCN} + \underset{417.0}{6\,(NH_3OH)Cl} + \underset{280.5}{5\,KOH} = \underset{(\cdot H_2O)\ 412.4}{K_4[(NO)Mo(CN)_5]} + 2\,N_2 + NH_3 + 6\,KCl + 12\,H_2O$$

The reaction is based on reduction with NH_2OH and disproportionation of the latter into NOH and NH_3. Thus, 5 g. of

MoO_3 powder is treated with 10 ml. of a solution of 25 g. of KOH in 20 ml. of water; the mixture is stirred to the point where everything just dissolves. A saturated aqueous solution containing 20 g. of KCN is then added and the mixture filtered through a medium-porosity fritted-glass funnel. Then, 17.5 g. of $(NH_3OH)Cl$ is added to the filtrate and the mixture stirred until the $(NH_3OH)Cl$ is dissolved. The red solution is now heated on a water bath for 30 minutes; then, an additional 10 ml. of conc. KOH is added. At this point, the red color changes to a light yellow and then slowly turns to violet. The appearance of the violet color is accompanied by the evolution of NH_3 and is quickly followed by the separation of the violet NO compound. The latter is collected (*after cooling*) by *filtration*, washed with alcohol and ether, redissolved in a minimum of hot water, and quickly filtered into cold, 50% potassium hydroxide. The deep-violet, crystalline compound reprecipitates (the mixture must sometimes be left standing overnight); it is washed with ethanol and ether and dried in vacuum. Yield: 40%.

PROPERTIES:

Hygroscopic; decomposes in air, becoming lemon-yellow. May be stored indefinitely under nitrogen; in vacuum, may be heated up to 180°C without decomposition or loss of water of crystallization.

Readily soluble only in water; insoluble in all the usual organic solvents such as ethanol, ether, benzene, acetone, pyridine, chloroform, CCl_4 and CS_2. The aqueous solution is quite unstable and decomposes after a short time with loss of color.

DropBooks

REFERENCE:

W. Hieber, R. Nast and G. Gehring. Z. anorg. allg. Chem. 256, 173 (1948).

Potassium Nitrosyl Cyanomanganate

$K_3[(NO)Mn(CN)_5]$

$$\underset{328.3}{K_3[Mn(CN)_5]} + 2\underset{139.0}{(NH_3OH)Cl} + 3\underset{168.3}{KOH} = \underset{332.3}{K_3[(NO)Mn(CN)_5]} + KCN + 2KCl + NH_3 + 4H_2O$$

A solution of 16.4 g. (0.05 moles) of $K_3[Mn(CN)_5]$ in 100 ml. of a 15% KCN solution is treated (in this order) with 7 g. of $(NH_3OH)Cl$

$(NH_3OH)Cl$ and a solution of 8.4 g. of KOH in 20 ml. of water. The mixture is then slowly heated, whereby it becomes brown, then violet. At this point flocculent $Mn(OH)_3$ appears occasionally due to hydrolytic cleavage of the $K_3[Mn(CN)_6]$. The end of the reaction is indicated by a dark-violet color of the solution and termination of the NH_3 evolution. After cooling, the solution is made weakly acidic by addition of acetic acid, and 18.5 g. of $Mn(CH_3CO_2)_2 \cdot 4\,H_2O$ in 60 ml. of water is added to give a copious but readily filtered rose-red precipitate of $Mn_3[(NO)Mn(CN)_5]_2$:

$$\underset{332.3}{K_2[(NO)Mn(CN)_5]} + 1^1/_2\,\underset{(\cdot 4\,H_2O)\ 367.7}{Mn(CH_3CO_2)_2} = {}^1/_2\,\underset{307.4}{Mn_3[(NO)Mn(CN)_5]_2} + CH_3CO_2K$$

The precipitate is carefully washed and digested with a solution of 35 g. of K_2CO_3 in 120 ml. of water:

$$\underset{307.4}{{}^1/_2\,Mn_3[(NO)Mn(CN)_5]_2} + \underset{207.3}{1^1/_2\,K_2CO_3} = \underset{332.3}{K_2[(NO)Mn(CN)_5]} + 1^1/_2\,MnCO_3$$

After slight heating the solution may be filtered, if necessary; it is then made weakly acidic with acetic acid, and a large excess of ethanol is added. On standing for a few days, the initially flocculent precipitate changes to fine, deep-violet crystals, which are collected and washed with ethanol. When kept over P_2O_5, the substance loses all water of crystallization and is converted to the anhydrous $K_2[(NO)Mn(CN)_5]$. Yield: 80–90%.

REFERENCE:

W. Hieber, R. Nast and E. Proeschel. Z. anorg. allg. Chem. 256, 167 (1948).

Sodium Nitrosyl Cyanoferrate

$$Na_2[(NO)Fe(CN)_5] \cdot 2\,H_2O$$

$$\underset{(\cdot 3\,H_2O)\ 422.4}{K_4[Fe(CN)_6]} + 6\,HNO_2 = H_2[(NO)Fe(CN)_5] + 4\,KNO_2 + NH_4NO_2 + CO_2$$

$$H_2[(NO)Fe(CN)_5] + Na_2CO_3 = \underset{(\cdot 2\,H_2O)\ 298.0}{Na_2[(NO)Fe(CN)_5]} + H_2O + CO_2$$

A 400-ml. beaker is used to dissolve 40 g. of $K_4[Fe(CN)_6] \cdot 3\,H_2O$ in 60 ml. of water (slight heating). Then, 64 ml. of nitric

acid (d 1.24) is added (stirring). The mixture is digested on a water bath at moderate temperature until a test drop of the brown solution reacts with $FeSO_4$ solution to give a dark green (rather than blue) precipitate. After standing for 1–2 days, the mixture is just neutralized with Na_2CO_3 (an excess must be avoided). The neutralized solution is heated to the boil, filtered and quickly concentrated to a small volume. After cooling, an equal volume of ethanol is added to precipitate most of the KNO_3. This is separated by filtration, and the solution is quickly reconcentrated to remove the ethanol. The dark-red solution yields crystals on standing; these are suction-filtered and washed with some cold water. Further crystalline material is obtained by repeating the evaporation of the mother liquors.

SYNONYM:

Sodium nitroprusside.

PROPERTIES:

Ruby-red orthorhombic-bipyramidic crystals. One part is soluble in 2.5 parts of water at 16°C.

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REFERENCES:

L. Vanino, Handb. d. präp. Chem. [Handbook of Preparative Chemistry], Inorganic Part, Stuttgart, 1925, p. 355; R. Wild, Arch. Pharm. 131, 26 (1865).

Sodium Carbonyl Cyanoferrate

$$Na_3[(CO)Fe(CN)_5]$$

Easily prepared via reaction of CO with $Na_3[Fe(OH_2)(CN)_5]$, which in turn is obtained from sodium nitroprusside.

a) $$\underset{(\cdot 2\,H_2O)\ 298.0}{Na_2[(NO)Fe(CN)_5]} + \underset{69.5}{(NH_3OH)Cl} + \underset{106.0}{Na_2CO_3} = \underset{272.9}{Na_3[Fe(OH_2)(CN)_5]} + \underset{58.5}{NaCl} + N_2O + CO_2 + H_2O$$

A solution of 20 g. of sodium nitroprusside and 10 g. of Na_2CO_3 in 80 ml. of water is prepared; the reaction flask is placed in ice and 7 g. of $(NH_3OH)Cl$ is some water is added. Gas evolution begins immediately and the solution turns a greenish brown. After one

hour, the product is precipitated as a brown tar with three volumes of ethanol. By repeated solution in water and reprecipitation with methanol, $Na_3[Fe(OH_2)(CN)_5]$ is obtained as a yellow powder. It is important to keep the temperature below 5°C to avoid formation of $Na_4[Fe(CN)_6]$ and iron hydroxides.

b) $\underset{272.9}{Na_3[Fe(OH_2)(CN)_5]} + \underset{22.4\,l.}{CO} = \underset{282.9}{Na_3[(CO)Fe(CN)_5]} + H_2O$

The freshly prepared aquo complex (13 g.) is dissolved in 35 ml. of boiled water and introduced into an evacuated three-neck flask fitted with a vacuum-tight mercury-seal stirrer, a dropping funnel, and gas inlet and outlet tubes. By repeated flushing and evacuation, the flask is filled with carbon monoxide (prewashed with an alkaline pyrogallol solution). When vigorously stirred, the solution starts to absorb CO at a fast rate; after 24 hours and absorption of 98% of the stoichiometric quantity of CO, the reaction is complete. The flask must be protected from light during the reaction. The product is precipitated from the greenish-blue solution by addition of 200 ml. of ethanol containing 0.5 g. of NaOH; it is filtered in air. After washing with some absolute ethanol, the complex is obtained in analytical purity.

Since $Na_3[(CO)Fe(CN)_5]$ is somewhat soluble in ethanol, it is recommended to work up the aqueous-alcoholic filtrate. To this end the filtrate is evaporated to dryness at 12 mm. and 40–50°C (bath temperature), the residue dissolved in the minimum amount of water, and all $Fe(OH)_3$ filtered out. The filtrate is concentrated to crystallization in a vacuum desiccator over conc. H_2SO_4; a very small quantity of mother liquor should remain. The crystals are collected by filtration, washed with some ethanol, and dried at 110°C. Yield: up to 90%.

PROPERTIES:

Pale-yellow needles, surprising stable.

REFERENCE:

W. Hieber, R. Nast and C. Bartenstein. Z. anorg. allg. Chem. 272, 32 (1953).

SECTION 5

Alloys and Intermetallic Compounds

G. BRAUER

General Remarks

The usual laboratory preparation of alloys consists of fusion of the metallic components. This method allows a simple control over the quantities of reagents so as to reach the desired composition. If the changes of the phase diagram of the metal system are known as a function of the temperature, this method also allows, in most cases, the preparation of definite intermetallic compounds. Occasionally, however, it is difficult to obtain the required homogeneity in the product because some of the reagents may burn, evaporate or react with the fusion vessel.

By comparison, other methods for the preparation of alloys are less used in the laboratory, although in special cases the optimum methods may involve reduction (chemical or electrolytic) of metallic compounds. In addition, some intermetallic compounds are best obtained as residues remaining after the corresponding basic alloys are dissolved. However, a knowledge of the temperature-induced transformations of the phase diagram is of the greatest importance in all cases; thus, the literature references below must be consulted, if at all possible.

Due to the enormous number of possible and known alloys and intermetallic compounds, a full description of all preparative methods is, of course, impossible. It is even less feasible to cite all the most important compounds separately. This section therefore contains only a selection of typical laboratory procedures; these are examples which may be adapted to other cases, even if the latter are unrelated. Only a few individual preparations are given in detail.

Further, it should be pointed out that preparative methods for metallic compounds overlap those for semimetals and nonmetallic compounds. For this reason, many of the methods cited here are derived from those for nonmetallic compounds; others, which stem from metallurgy, may also be applied to other substances.

REFERENCES:

Collected phase diagrams of metallic systems:

M. Hansen and K. Anderko. Constitution of Binary Alloys, New York-Toronto-London, 1958; Landolt-Börnstein. Zahlenwerte und Funktionen [Numerical Values and Functions], Vol. II, Part 3, 6th Ed., Berlin-Göttingen-Heidelberg, 1956; W. Hume-Rothery et al. Metallurgical Equilibrium Diagrams, London, 1952; E. Jänecke. Kurzgefasstes Handbuch aller Legierungen [Short Handbook of Alloys], Heidelberg, 1949; T. Lyman (Amer. Soc. Metals). Metals Handbook, Cleveland, 1948 (Binary and Ternary Alloys); J. L. Haughton. Bibliography of the Literature Relating to Constitutional Diagrams of Alloys, London, 1942; M. von Schwarz. Metall- und Legierungskunde [Metals and Alloys], Stuttgart, 1929 (Binary, Ternary and Quaternary Alloys).

Preparation of Alloys by the Use of Heat

Purity of the Starting Materials

Except for special cases where some purification is achieved by the vaporization that occurs at relatively high temperatures, one should not expect that the product alloys will be purer than the starting metals. Therefore, the latter should be as pure as possible and should contain a minimum of dissolved impurities ("internal" impurities). The "external" impurities also cannot be neglected. Thus, oxide layers must be removed by scraping or grinding, or by chemical etching with suitable acids. Industrial metals comminuted by mechanical means (powders, shavings) are frequently contaminated by traces of lubricants. These must be removed by extraction with organic solvents; otherwise, they tend to interfere with the alloy formation and form carbides. Water and all organic solvents must be removed by careful drying.

The optimum methods sometimes involve metal hydrides rather than pure metals. The procedure is useful mainly in the case of metals that form stable hydrides (alkali and alkaline earth metals, *Ti to Th*, *V to Ta*, *Pd*). The hydrides are readily reduced to powders and the contact of the latter with the other components of the alloy is much better than it would be otherwise. The thermal decomposition of the hydrides proceeds so easily that the formation of alloys is not only not slower than in the case of pure metals, but is faster due to the small particle size of the material. In addition, the hydrogen liberated from the hydride may reduce the oxide impurities. One disadvantage inherent in the use of hydrides is that the commercial materials are usually less pure than the corresponding metals.

Form of the Starting Materials

The starting material may consist of chunks, ingots, shavings or powders. Large chunks have relatively small surface areas, thus introducing fewer "external" impurities; they usually leave less material on the container walls. On the other hand, mixtures of large chunks may sometimes be difficult to reduce to a homogeneous melt, especially if the components of the alloy differ greatly in density or melting points. While homogeneous mixtures of powders already in the solid state can be prepared, the oxide skin frequently prevents junction of the particles even when sufficient heat is applied; in addition, powders have a greater tendency to cling to the container walls, again because of surface oxides. The metal hydrides may be found advantageous in this case, as mentioned above. The formation of alloy from powders, shavings or thin wires is greatly improved by pressing the mixture into pellets prior to heating (suitable dies are described in Part I, p. 103). (They are made from shape-retaining "oil-tempered" steel and are hardened only after machining and careful fitting of the die and the matrix.)

Metals which readily acquire a surface oxide layer may be cut into a potlike shape on a lathe. The other alloy components can then be hammered into the hollow to assure an intimate contact from the very start.

When two components with widely differing melting points are fused, the fusion pot should be arranged so that the lower-melting metal must run through the higher-melting one.

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Preparation of Starting Mixtures

It is desired to obtain the desired alloy composition by weighing out theoretical quantities of the components but, for various reasons, this composition cannot always be achieved that simply. Frequently a number of successive preliminary experiments must be carried out, whereby one gains the necessary experience.

The most important causes of deviation of the product from the desired composition are losses of metal by vaporization, oxidation or side reactions with the material of the fusion pot. In such cases the expected losses of a component are balanced by adding an extra quantity of that component to the starting mixture. A rough approximation of the extra quantity required is obtained from the fact that when the preparation is conducted properly and in closed crucibles (see below), not even the very reactive mixtures of alkali metals lose more than 5% of the starting weight.

An especially clean way to measure out alkali metals consists in melting the latter in small, sealed glass ampoules, from which they can easily be removed by remelting (see the section on Alkali Metals, pp. 961-967).

Crucible and Ampoule Methods

The alloy components, weighed out with the above considerations in mind, are combined by fusion in crucibles or ampoules. Some method must always be devised to minimize losses due to burning or vaporization. In simple cases, where open vessels are used, this is achieved by covering the charge with a protective layer of a salt or salt mixture which also melts in the process. Alternatively, the mixture may be protected by a blanket of an inert gas; crucibles may be closed by a lid and ampoules by fusing the constricted neck. If the closure is gas-tight, some inert or reducing gases may be included and a vacuum may even be maintained.

Several low-melting salts and salt mixtures suitable for laboratory use are given in Tables 1-3 (for further references, see Guertler [1]). Many such protective agents are commercially available for industrial use and they can also be employed.

Table 1

Melting Points of Some Salts Suitable for Use in Protective Layers

Salt	M.p., °C	Salt	M.p., °C
$LiNO_3$	255	LiF	870
$NaNO_3$	307	Na_2SO_4	884
KNO_3	334	KBO_2	947
LiCl	613	$BaCl_2$	962
$MgCl_2$	708	$NaBO_2$	966
$Na_2B_4O_7$	741	K_2SiO_3	976
$CaCl_2$	772	NaF	988
KCl	776	Na_2SiO_3	1088
NaCl	801	CaF_2	1360
KF	880		

Hygroscopic salt mixtures sometimes react with the molten alloys, evolving hydrogen and interfering in the reaction. This effect can be reduced by adding KOH.

The type of protective atmosphere depends on the metals of the alloy. Hydrogen is frequently used, except when large quantities of hydride-forming alkali, alkaline earth or rare earth

Table 2

Melting Points of Some Binary Salt Mixtures with Uniform Melting Points

Wt. %	Salt I	Wt. %	Salt II	M.p., °C	Wt. %	Salt I	Wt. %	Salt II	M.p., °C
73	KNO_3	27	$LiNO_3$	132	32.8	KCl	67.2	$BaCl_2$	645
55.3	$NaNO_3$	44.7	$LiNO_3$	208	51	$LiBO_2$	49	$NaBO_2$	648
46	LiCl	54	KCl	352	77.8	NaCl	22.2	$BaCl_2$	654
57	LiCl	43	KCl	550	45	NaCl	55	KCl	660
61.4	KCl	38.6	$MgCl_2$	426	35.8	LiF	64.2	MgF_2	669
44	NaCl	56	$MgCl_2$	430	72	NaCl	28	NaF	675
12	LiF	88	LiCl	485	51	KCl	49	K_2SO_4	690
32.8	NaCl	67.2	$CaCl_2$	500	50	Na_2CO_3	50	K_2CO_3	690
33.7	NaCl	66.3	LiCl	552	32.4	NaF	67.6	KF	700
45.8	KF	54.2	AlF_3	565	35.4	LiF	64.6	AlF_3	710
73.5	KCl	26.5	$CaCl_2$	600	63.7	LiF	36.3	AlF_3	715
44.2	Na_2SO_4	55.8	Li_2SO_4	601	52.8	NaF	47.2	CaF_2	810
63	KCl	37	KF	605	61	NaF	39	MgF_2	815
35	NaCl	65	Na_2CO_3	620	21.5	NaF	78.5	MgF_2	985
46.6	NaCl	53.4	$Na_4P_2O_7$	620	90.4	KF	9.6	AlF_3	835
32.8	NaCl	67.2	Na_2SO_4	623	87.8	BaF_2	12.2	MgF_2	890
26	KCl	74	$CaCl_2$	640	78.8	BaF_2	21.2	MgF_2	930
85	$CaCl_2$	15	CaF_2	644					

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metals are present; in other cases, nitrogen is used, except when nitride-forming Li, Be, Mg, Ca, Sr and Ba, or the rare earth metals, Ti, Zr, Hf, Th, V, Nb and Ta are present. If no carbides can form, CO may be used to advantage; however, CO_2 and SO_2 may occasionally oxidize the metals at high temperatures. Noble gases, especially argon, which is commercially available in cylinders at 150–200 atmospheres pressure, are the best but also the most expensive protective agents. For real protection the gas should be very pure: oxygen is undesirable even in traces. Gas purification methods are given in various sections of this handbook (H_2: p. 111 ff.; N_2: p. 457 ff.; noble gases: p. 82 ff.). Occasionally, H_2, N_2 and Ar are available in high purity (99.99%) from commercial sources, sometimes on special order.

High, narrow crucibles are preferred. Useful crucible materials are a) metals, b) ceramics and c) glasses (for ampoules).

A) METALS:

For obvious reasons, only high-melting metals which do not tend to form alloys are suitable for crucibles. Iron and various types of steel, as well as molybdenum and tantalum, are frequently used. Molybdenum is very serviceable but also much more expensive and less easily worked than Fe. These metals are preferentially used for smelting alloys of the "B" group of

elements and for the extremely reactive alkali and alkaline earth metals (see Table 4).

Table 3

Melting Points of Some Ternary Salt Mixtures with Uniform Melting Points

Wt. %	Salt I	Wt. %	Salt II	Wt. %	Salt III	M.p., °C
16.4	NaCl	24.6	KCl	59.0	$BaCl_2$	540
76.4	$BaCl_2$	14.0	KCl	9.6	Na_2CO_3	542
24	NaCl	37	KCl	39	Na_2CO_3	580
5	NaCl	9	KCl	86	$Na_2B_4O_7$	640
53.3	AlF_3	13.2	CaF_2	33.2	NaF	705
10.1	AlF_3	34.4	CaF_2	55.5	NaF	760
15.9	AlF_3	26.7	CaF_2	57.4	NaF	825
20.5	AlF_3	51.7	CaF_2	27.8	NaF	1095

Table 4

Metallurgical Classification of Elements

																H	He
Li											Be	B	C	N	O	F	Ne
Na											Mg	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	X
Cs	Ba	R.E.	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Em (Rn)
Fr	Ra	Ac	Th	Pa	U												
Alkali- and alkaline earth metals		Transition metals									B Elements						

Metallic Pt, Ag and Ni, which are normally chemically inert and thus are used as vessel materials under corrosive conditions, cannot be used in crucibles because of their intrinsic and pronounced tendency to form alloys.

The preparation of alloys of the so-called transition metals virtually always requires ceramic crucibles (see also below).

A gas-tight seal for an iron crucible can be obtained in a number of ways. An iron lid may, for instance, be put on and sealed in place by means of flanges; the lid may also be in the form of a threaded cap or plug, which yield a firmly closed circular seal. Two types of screw caps are shown in Fig. 273, p. 990. Tubular crucibles with fitting lids (or plugs) can frequently be welded shut for a gas-tight seal. In this case, the plug closely fits the I.D. of the crucible and has the shape of a tube with one end closed. Examples of this are given in Fig. 347. Even though the crucible may contain a protective gas blanket, the gas-filled space above the material to be alloyed should be kept at a minimum. With this in mind, the inner cylinder serving as a plug in the crucible of Fig. 352b should be hammered down (after charging) as far as possible, sawed off near the rim of the outer crucible and then welded to the outer rim. A plug shaped as a hollow cylinder is easier to weld at the rim than a solid plug. The hollow plug should be slightly tapered (into a cone) near its upper rim. Alternately, its rim should be turned down slightly after it is driven in (it thus forms a flange surface). In either case, the aim is to close off the seam and prevent welding gases from penetrating into the crucible. If generation of a large amount of heat is expected on welding and if it is undesirable to trigger the reaction until the crucible is tightly sealed, its lower section may be cooled in water during welding. This would have to be done, for instance, in welding crucibles containing the very volatile alkali and alkaline earth metals when they are to be alloyed with "B" metals.

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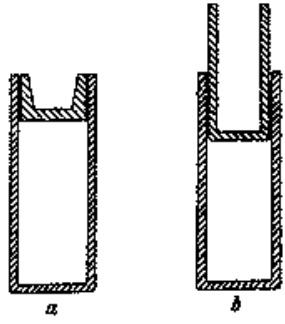

Fig. 347. Tubular steel crucible. When small quantities of alloy are needed (for instance, in crystal structure studies) the following dimensions have proved useful: O.D. 20–25 mm., wall thickness 1–2 mm., height 70–90 mm.

Prior to closure of the crucible, the protective gas may be introduced through a narrow tube. A better method is to put the charged crucible, with the lid loosely in place, into a large-diameter glass tube, which is closed at one end and fitted with a ground glass joint and stopcock (Fig. 348). The tube is then alternately evacuated and filled with the protective gas. This arrangement displaces the air very efficiently.

Fig. 348. A method for evacuating a metal crucible and filling it with a protective gas blanket.

After fusion and cooling, the iron crucibles are opened by sawing off the top and bottom, and the alloy is then punched out of the open cylinder. In another method, the crucible is placed on a lathe, clamped at the stopper end, and its wall turned down to 0.1–0.3 mm. This thin wall can then be stripped off with a pair of pliers in the same manner as the top of a can of sardines. Since this can be done very rapidly, even those alloys which are very sensitive to air can be isolated without too much damage and can be rapidly transferred to a storage vessel filled with a protective gas. The method is also useful in cases where the alloy ingot adheres firmly to the crucible walls because of local welding.

Alloys which are extremely sensitive to air, especially those with high concentrations of alkali and alkaline earth metals, require special methods for the removal of the ingot from the iron crucible [2]. In the device of Zintl and Harder (Fig. 349) a tubular iron crucible can be opened while completely surrounded by a protective gas.

The iron tube r is connected via the standard-taper joint s to a source of pure N_2 as well as to other devices for further treatment of the alloy. The tubular crucible t, whose wall has already been machined down on a lathe (see above) so that it is now thin, is positioned in r by means of the screws a in such a way that its bottom may be sawed off through the slit c while still under N_2 (the length of the circumferential slit c is equal to only 2/3 of the diameter of tube r). After the crucible bottom is sawed off, the crucible is pushed to the right by means of a thick wire (which passes through an axial hole in the cover plate e) and repositioned by means of screws a. The top of the crucible (that is, the plug) is now sawed off; the cover plate e is taken off for

a moment and the debris removed. The alloy is now contained in an iron tube (casing) which is open at both ends. The iron filings still adhering to the tube and ingot are tapped out. The alloy can now be pushed out of the casing by a steel rod passed through the hole in *e*. In certain cases the casing tube (including the alloy inside) may be used directly in further workup, e.g., an extraction. The protective gas should escape through only one hole at a time; the slit *c* for the saw can be closed off by collar *d*, the hole in *e* by means of a rubber stopper. This apparatus was originally used for the preparation of Na–Pb and Na–Sn alloys.

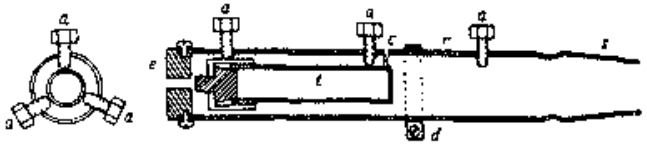

Fig. 349. Opening of a tubular iron crucible in the absence of air. *r* iron tube with standard-taper joint *s*; *t* crucible; *a* screws to fasten the crucible in place (nine such screws are arranged, in groups of three, along the circumference of *r*, the angles between the screw axes being 120°, as indicated in the insert); *c* slit for the introduction of a hacksaw; *d* collar for closing the slit when not in use; *e* cover plate for the tube *r*.

DropBooks

In the arrangement of Klemm and Dinkelacker, described in greater detail in Fig. 353 and on p. 1788 f., complete removal of the ingot from the tube is unnecessary; only quantities needed for immediate use need to be drilled out.

B) CERAMIC MATERIALS

Crucibles made of various kinds of ceramic materials can be used. The reader is referred to the text and tables in Part I, p. 12 ff., especially Table 7. Recently, crucibles of Ce and Th sulfides have proved advantageous for the fusion of nearly all metals, the exception being Pt. They can be used up to 1800°C [3].

Crucible shapes frequently used in the study of alloys are the conical (the so-called high shape) and the long, cylindrical (Tammann tubular crucible), both with a rounded or, less frequently, a flat bottom. Ceramic crucibles may be fitted with lids of the same material, but these can usually not provide a gas-tight seal by themselves (some sealing compound must be provided). Only alumina (Al_2O_3) can be fused and then only in the case of very small tubular crucibles (about 15 mm. O.D.). In this case a well-fitting plug may be fused to the crucible wall with an

acetylene-oxygen flame (welding torch) [4]. Thus, a crucible of the type illustrated in Fig. 350 is charged to a quarter of its height with the metal, closed off with the loosely fitting plug, and evacuated and filled with a suitable inert gas in the apparatus of Fig. 347. The crucible is then surrounded by moist sand to one half of its height, and the top section, including the plug, is carefully heated, using first a city gas-air mixture, then the acetylene-oxygen flame. The flange of the plug eventually fuses to the rim of the crucible (m.p. of Al_2O_3 = 2050°C). The entire closed crucible is then cooled carefully and uniformly. Some experience is necessary to avoid cracking during the fusion and, especially, during the cooling.

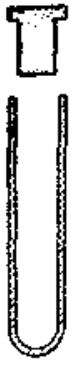

Fig. 350. Tubular alumina crucible. O.D. about 15 mm., length 65 mm.

Tubular crucibles made of Pythagoras mass* may be closed off in the same way as an ampoule, that is, by pulling to a small diameter and sealing the top end in a hydrogen-oxygen or acetylene-oxygen flame (see ampoule methods, p. 1782).

In another method, the crucible is lined with other materials. This method allows using, in the preparation of alloys, chemically resistant materials that cannot be shaped like a ceramic when unsupported.

Thus, CaO linings are suitaibe for work with Ca alloys and, in general, with calcium metal, which is extremely corrosive when hot. The Jander method of lining iron crucibles with CaO (already mentioned in Part I, p. 13) consists of the following.

The crucibles are 12 cm. high and 2.5 cm. I.D., with a wall 1 mm. thick. A thick paste of freshly prepared quicklime (from precipitated $CaCO_3$) and water is partly poured in and partly painted on the inside of the crucible so that there is a layer 1–2 cm. thick at the bottom and a wall lining 0.3–0.4 cm. thick. Rotating the crucible and careful pressing with a spatula produce a good and even coat. The crucible is then very slowly dried at room temperature or at 30–40°C; any cracks that appear are filled by pressing with a spatula (this can be done as long as the cake is

*Pythagoras mass is a low-melting porcelain used for laboratory ware and electrical resistor casings, useful for temperatures not exceeding 1500°C. Its melting point is about 1730°C (Houben-Weyl, Allgemeine Laboratoriumspraxis [General Laboratory Practice], 4th ed., part 2, Georg Thieme Verlag, Stuttgart, 1959, p. 634).

still moist). Cracks that appear after this cannot be remedied; very fine cracks do no harm, as experiments with cracked CaO linings have shown. After the initial drying the temperature is increased to dark red heat, which transforms the $Ca(OH)_2$ to CaO. Dry CaO does not adhere well to iron. Since its coefficient of expansion differs from that of iron, the crucible must be heated very carefully and treated very gingerly even after the lining process. The crucible is charged with the reactants, and an iron lid, also coated with CaO, is welded on.

Coatings of LiF are suitable for work with lithium alloys and metallic lithium at temperatures below 800°C. These coatings adhere relatively well to zirconia (ZrO_2) crucibles [6]. Thus, several grams of LiF (m.p. 870°C) are placed in a ZrO_2 crucible which is positioned in a small, movable electric furnace. The crucible is firmly seated in the furnace by means of asbestos wool. A clear melt is produced on heating; the current is then shut off and the melted LiF evenly distributed over the crucible walls by tilting the furnace. This is continued until the crucible cools sufficiently for the material to set. Afterward, the furnace is allowed to cool slowly at a low current (from 700°C to 300°C in one hour). The lithium fluoride lining thus formed has a thickness of 1–2 mm. If the cooling is too rapid, it will have large cracks; small cracks are nearly unavoidable, but are not deleterious because of the high surface tension of most metals.

Other lining materials, such as Nucerite, which can be directly bonded to metals, under certain conditions withstands temperatures up to 650°C, and is resistant to many gases, are also on the market. In addition, such materials as Pyroceram will be quite useful in the high-temperature laboratory.

Of late, many new ceramic materials have been developed for use in the various military and space programs. It is not possible to list them in this short section. Besides, this field is undergoing very rapid changes and new materials appear almost monthly. The reader is therefore advised to spend some time consulting the pertinent trade literature before proceeding with the experiment. He may find such investment of time very worthwhile, because it may result in a simpler, better, more convenient and cheaper experimental arrangement.

Ceramic crucibles may also be placed in glass, quartz or ceramic combustion tubes (one end open) so that the material may be in a vacuum or an inert gas atmosphere during the heating. Such an arrangement is shown in Fig. 272, p. 984.

Ceramic crucibles are frequently enclosed in slightly larger iron crucibles, which are then hermetically sealed with a welded-on plug; this arrangement combines the chemical resistance of ceramics, especially the oxides of Be, Mg, Al, Zr and Th, with the ease of sealing of iron crucibles.

Finally, all the crucible types mentioned above may be sealed into glass ampoules: this permits maintaining a vacuum or a desired gas atmosphere during the fusion.

C) AMPOULES

All types of glass, especially the high-melting glasses (see Part I, p. 5 ff.) and quartz, as well as tubes of Pythagoras mass, can be formed into ampoules (bomb tubes) and used for alloying of metals by fusion. The glass type used depends on the maximum working temperature. Pyrex can be used up to 560°C, Vycor up to 800°C under normal conditions and 1100°C for a short time, fused silica up to 1150°C, and Pythagoras mass up to 1400°C without danger of deforming. The metal reactants are changed into a long combustion tube of the appropriate ampoule material. The tube will normally have an I.D. of 10-20 mm., a wall thickness of 1.5-2 mm., and a round bottom of uniform thickness. The tube must be thoroughly cleaned and dried. It is then constricted just above the charge, but not so close to the latter that a reaction will be set off by the heat applied during sealing. The wall must be fairly thick at the constriction. The tube is evacuated and sealed at the constriction, thus forming an ampoule containing the metals under vacuum. The constricting and sealing are done with suitable torches (city gas-air, H_2-O_2, etc.), depending on the softening temperature of the ampoule material.

The ampoule can also be filled with a protective gas. However, the thermal expansion of the gas must be taken into account in this case. For this reason, the ampoule is filled with the requisite gas at less than atmospheric pressure at room temperature.

After fusion and resolidification, the ampoule is broken up and the metal ingot isolated. The composition of the alloy may then be calculated (approximately) from the weights of the reactants and the product. However, only careful chemical analysis can give the true composition.

Heating and Cooling

The required reaction or fusion temperature is determined from the phase diagram. As a minimum, this temperature must be higher than the liquidus point of the alloy product. Preferably, however, it should exceed the melting points of all the reacting metals. The best temperature is one which exceeds the liquidus point by 30-50°C over the entire range of compositions of the system. Such a temperature will certainly ensure proper reaction conditions.

Heat sources may be furnaces of various types (see Part I, pp. 32-42). In general, the materials may be heated up as

rapidly as desired. The temperature increase due to the heat of reaction may be neglected. The heating time should be as short as possible to avoid reactions between the metal and walls of the reactor, and should in no case be longer than the time absolutely necessary to achieve a uniform composition. For this reason, the furnace should be preheated to approximately the desired temperature prior to the introduction of the vessel with the reactants. This vessel must, of course, be heated slowly enough to avoid stresses which would produce breakage. This applies particularly to glass ampoules and ceramics of low thermal conductivity. In any case, well-designed protective glasses or goggles must be worn during these operations.

When the desired melting temperature is reached; the homogenization of the mixture is promoted by mechanical means. Open crucibles are stirred with a rod of suitable material; tightly closed vessels (crucibles with a screwed-on or welded-on lid, ampoules) are taken out of the furnace and shaken or tumbled a few times; in the case of crucibles which are open but surrounded by a second protective vessel and which thus cannot be shaken or tumbled, at least some motion of the melt can be induced by external tapping or vibrating. All such agitation procedures must be followed by a short reheating to the maximum desired temperature.

Cooling also depends on the phase diagram as well as the intended use of the alloy. If there is no danger of separation of mixed crystals (with subsequent alteration of the composition of the alloy) and no peritectic reactions are expected, or if the composition achieved at the high temperature is the one desired in the solid, the material is quickly cooled in air. Materials in metal or quartz vessels may also be quenched in water or oil.

On the other hand, when a reaction must be completed at a lower temperature or it is desired to produce single crystals for studies on structure, then a slow, controlled reduction of the temperature is required. The type of cooling procedure thus depends on the application.

The formation of large single crystals from the melt may be favored by quiet, vibrationless cooling. Sometimes, however, motion of the melt during crystallization is desirable. The heating and cooling methods used for single crystals of pure metals are also applicable to single crystals of intermetallic compounds that exhibit congruent melting (see Part I, p. 94 ff., and [7]).

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5. W. Jander. Z. anorg. allg. Chem. 138, 321 (1924).
6. E. Zintl and G. Woltersdorf. Z. Elektrochem. 41, 876 (1935); E. Zintl and G. Brauer. Ibid. 41, 102 (1935).
7. O. Buckley. Crystal Growth, New York-London, 1951; W. D. Lawson and S. Nielsen. Preparation of Single Crystals, London, 1958; W. G. Pfann. Zone Melting, New York, 1958; R. O. Grubel. Metallurgy of Elemental and Compound Semiconductors, New York-London, 1960.

Alloy Synthesis under Pressure

Special methods are required when one of the constituent metals of the alloy has a very low boiling point (Zn, Cd, Hg; see also p. 1789) while the other constituent has a high melting point (platinum metals and other transition metals; see Table 4, p. 1776). In this case, if the pressure is atmospheric pressure, one metal tends to vaporize before the other liquefies. Nowotny et al. have designed a special furnace which allows heating such metal combinations in a protective gas at high pressures. The apparatus is essentially a closed iron bomb containing a resistance-heated tube which encloses the crucible (*Fig.* 351). The furnace mantle *m* is a thick-wall seamless steel tube whose lower section is threaded for 50 mm. and carries a screw cap *v*. This cap in turn carries a threaded adapter which is connected to the compressed gas cylinder, the pressure gage and one of the two electrical terminals. All screw connections are also sealed with lead gaskets *b*. The other end of mantle *m* is closed off by cover plate *d* (a 35-mm.-thick circular steel plate) held in place by flange *f* and connected to the second electrical terminal. The gasket ring *r* is made of insulation-grade asbestos, and the six flange screws are of high-strength nickel-chromium steel (the screws must also be insulated from the flange by sleeves and washers of electrically insulating asbestos or similar material). The inner walls of plate *d* and the cap *v* are threaded so as to support the brass collars h_1 and h_2. The latter make the electrical connection between the plate and cap and the carbon resistance element which they support. To obtain good electrical contact between the brass collars and the carbon sleeve conductors g_1 and g_2, the I.D. of the collars is made 0.1 mm. smaller than the O.D. of the corresponding section of the carbon sleeve. The collar is then heated and slipped over the

sleeve while still hot. The heating tube k is made from electrographitized carbon and has a wall thickness of 1.5–1.8 mm. in the long middle section and 4 mm. at the ends. Its ends fit tightly into sleeves g_1 and g_2.

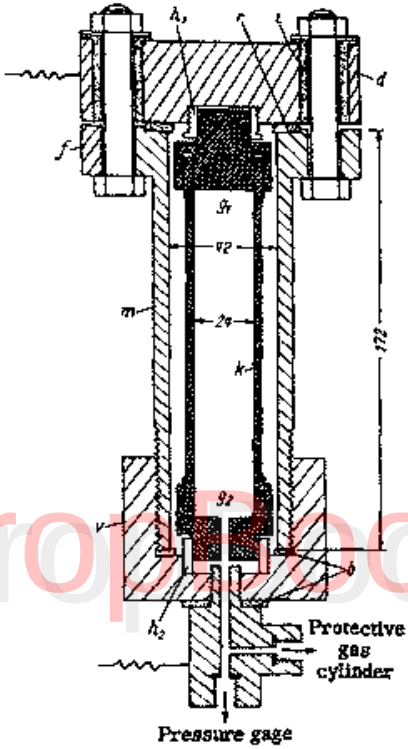

Fig. 351. Tubular furnace for high temperature pressure synthesis. k carbon tube; g_1, g_2 special carbon sleeve conductors; h_1, h_2 brass collars; m outer steel tube (mantle); f flange; d cover plate; v screwed-on cap; b lead gaskets; r, i asbestos gasketing rings and sleeves. Dimensions in mm.

The narrow, high tubular crucible containing the charge is centered in k. The furnace is connected to a low-voltage transformer capable of delivering 600–900 amp. at 12 volts. The apparatus is filled with a protective gas (N_2 or Ar) to 60–70 atm.; the pressure increases rapidly to about 150–200 atm. during heat-up but then decreases again during the actual fusion (it drops to about 70–100 atm. in 10 min.). The temperature cannot be measured directly;

it can only be estimated from the current consumption, assuming otherwise constant conditions (preliminary experiments are helpful). During the run, the furnace is immersed in running water up to the flange while the lid is cooled by spraying water from above.

Electrographitized carbon is a useful crucible material for preparation of alloys of Zn and Cd with Pt or Pd. Alumina crucibles do not last. The volatile-metal loss may approach 25%. The carbon tube and sleeves may last for 40-70 fusions (10 minutes each). Obviously, this furnace is not suitable for metals which readily form stable carbides.

REFERENCE:

H. Nowotny, E. Bauer and A. Stempfl. "Alfons-Leon-Gedenkschrift" der Allg. Bau-Zeitung, Vienna, 1951, p. 63.

Melting Without a Container

Under certain conditions it is possible to melt small quantities of metals, alloys and related compounds in such a way that they do not make or barely make contact with the wall of the container. Such a procedure becomes very desirable when one deals with corrosive elements or when products of very high purity are required. However, "containerless" fusion is possible only in special cases. For example, the sample may be heated to melting by means of an electric arc or a directional electron beam; in this case the sample rests in a shallow depression in a cooled copper plate. The molten sample contracts due to surface tension to form an oblate spheroid whose area of contact with the copper support is so small that no contamination occurs during the short fusion process. The resolidified sample is turned over and remelted on the other side. This procedure is called button melting. For heat sources, see Part I, p. 42.

Another melting method is the so-called levitation melting in which the sample is freely suspended in vacuum or in an inert atmosphere by a field developed by means of induction coils, which also supply the heat. This promising method is, however, still in the experimental stage. [E. C. Ocress, D. M. Wroughton, G. Commetz, P. H. Brace and J. C. R. Kelly, J. Appl. Phys. 23, 545 (1952); J. Electrochem. Soc. 99, 205 (1952)].

Comminution in the Absence of Air

Special precautions must be taken while studying alloys that are extremely sensitive to air, hygroscopic or readily oxidized. This

is especially true of operations in which one is trying to obtain comminuted material, shavings, etc., for density determinations or x-ray powder diagrams, where such material must be completely free of decomposition products. Devices for producing such comminuted alloys have been developed by Zintl et al. (I) and Klemm and Dinkelacker (II).

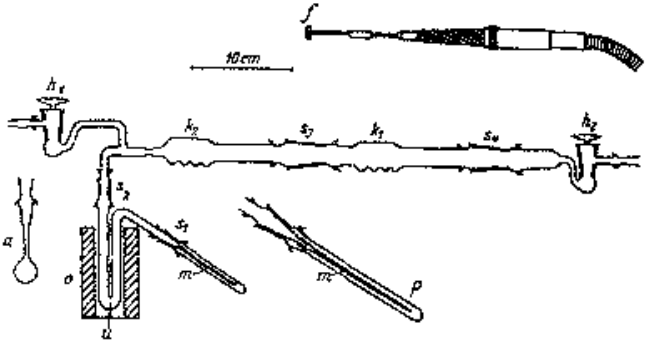

Fig. 352. Comminution of sensitive alloys in the absence of air. k_1, k_2 working chambers for handling the alloy; h_1, h_2 high-vacuum stopcocks; m capillary for x-ray sample; u glass tube for annealing the alloy powder; o electric furnace; a adapter with the analysis and sample storage bulb; f rotary milling tool.

I. The apparatus in Fig. 352 consists of several glass parts connected by ground joints s_1–s_4. The assembly is connected via Schiff stopcocks h_1 and h_2 (see Part I, p. 59 f.) to a high-vacuum pump and a supply of pure, anhydrous inert gas.

The major constituent parts of the apparatus are two slightly oblate chambers k_1 and k_2 made of medium-wall glass tubing. The underside of each chamber carries three to four corrugations impressed with a carbon rod on the hot, soft tube. These corrugations prevent the alloy from slipping out of the chamber during workup. Depending on need, devices for annealing the comminuted material, for charging the glass capillaries which are used to hold the sample while examining its x-ray powder pattern, or for removal of analytical samples (analysis bulbs) may be added.

Before use, the entire apparatus is thoroughly evacuated over a period of several hours. At the same time, it is carefully heated (to promote removal of moisture) and then connected via stopcock h_1 to the protective gas supply. The blanketing gas is allowed to escape at h_2. A small piece of the solid alloy is then introduced into chamber k_1 via the ground joint s_4. A fast stream of the

protective gas is maintained while introducing the sample, following which a loosely fitting rubber cap is put over joint s_4. This permits the gas to escape while preventing air penetration into k_2. The surface of the alloy in k_1 is cleaned by means of a small rotary milling tool f (5 mm. O.D.), set on a 12-cm.-long rigid shaft and introduced via s_4. The rigid shaft is attached to the chuck of a flexible shaft driven by a dental drilling machine. The alloy piece is cleaned on all sides and is then pushed into the chamber k_2 by means of a thick wire or a thin glass rod. The powdered waste material removed from the metal surface must not be entrained from k_1 into k_2 (it can be dislodged from the metal surface by tapping).

When the material is safely in k_2, k_1 is disconnected at s_3. The required quantity of clean shavings is then produced from the alloy in k_2 (a new, clean milling tool should be used). After this, s_3 is reconnected to k_2. Turning and tapping the assembly transfers the fresh alloy shavings (or powder) to tube u (this tube must be prebaked and degassed in high vacuum). The alloy powder in u may then be annealed in the heat produced by furnace o. This treatment removes stresses and is frequently necessary in order to obtain good powder patterns with sharp interference peaks. If very sensitive alloys are handled, the temperature maintained during degassing of tube u must be higher than during the succeeding annealing of the sample. After the annealing, the required quantity of powder is transferred to the capillary tubes m, which are then melt-sealed prior to introduction into the x-ray powder pattern analyzer (the wide end of tube m is cemented to the adapter at s_1, and a small side opening serves to equilibrate its pressure with that in the protective tube p).

If desired, tube u may be replaced by a bulb for sealing off analytical samples. The net weight of the empty bulb and its adapter (to s_2) is first established. The bulb is then filled with alloy powder and sealed off. It is then reweighed, and the total weight of the oxide-free metal powder can thus be accurately determined.

ff. The arrangement of Klemm and Dinkelacker also utilizes a small rotary milling tool for cleaning of the surface and comminution of the alloy chunk. In this method, however, the alloy is not removed from the crucible but is powdered while still in the crucible. The apparatus is shown in Fig. 353.

The thick-wall brass shell a houses vessel b, which can be rotated on axis t. The top of the crucible containing the freshly prepared alloy is sawed off, and the crucible is introduced via the ground-joint adapter c, which slopes upward. The crucible is then firmly fastened in b by means of a small screw r. Vessel b can be turned into any desired position by means of handle d. It is then fixed in that position by turning down screw s, which thus

immobilizes axis *t*. Housing *a* can be evacuated via the ground-metal joint *f*, while additional vessels for further treatment of the alloy (analysis, powder pattern, density determination, etc.) can be attached at a similar joint *e*. The apparatus can be completely sealed and evacuated if handle *d* is taken off and a standard taper cap pushed over the ground joint *g*.

The surface of the alloy in the crucible is cleaned by means of a small, rapidly rotating steel milling tool (5 mm. diameter), driven from a dental drill via a flexible shaft and introduced through joint *c*. The impurities removed from the surface of the alloy are dumped into *c* by turning *b* on axis *t*. A disposable rubber wiper blade *w* cleans off all waste powder from the walls of *a* and pushes it into *e*. The waste is then removed from *c*, the joint is cleaned by blowing through it inert gas, and a new cutting tool is introduced through *c*. The clean alloy shavings (see the previous method) thus produced are removed through *e*.

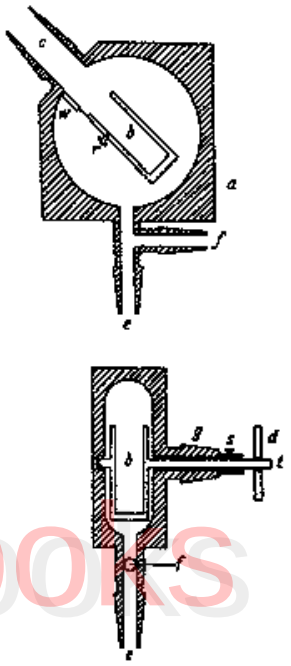

Fig. 353. Comminution of alloys in the absence of air without removing the alloy from the crucible. *a* brass housing; *b* vessel housing the crucible and able to rotate; *t* axis on which *b* rotates; *d* handle; *w* rubber wiper blade for scraping off loose particles.

DropBooks

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Distillation Method

If one component of a desired binary alloy is more volatile than the other and if the decomposition vapor pressure of the alloy is not too high, the alloy can be prepared by distilling or subliming the volatile component onto the other.

However, apart from a few exceptional cases this method is, for obvious technical reasons, restricted to alloys made of relatively volatile metals and metalloids, that is, those boiling below 1000–1100°C at 760 mm. This is because distillation at higher temperatures is quite difficult in practice. (However, much less volatile

metals can be distilled in small amounts in high vacuum.) The method is therefore suitable for:

Na, b.p. 880°C,	Mg, b.p. 1107°C,	P, b.p. 280°C,
K, b.p. 760°C,	Zn, b.p. 907°C,	As, b.p. 615°C,
Rb, b.p. 700°C,	Cd, b.p. 767°C,	Se, b.p. 688°C.
Cs, b.p. 670°C.	Hg, b.p. 357°C,	

The special advantages of the distillation method are as follows:

a) The volatile component is repurified by the distillation just prior to the reaction (this is important in the case of very reactive metals).

b) The reaction between the vapor of one component and the powder of the other proceeds quietly and smoothly (because of the limited amount of vapor present at any time).

c) Any excess of the volatile component can be distilled off after the reaction.

Each of the components is placed in a separate boat and the boats are positioned one behind the other in a horizontal tube. The choice of boat and tube materials is governed by the same considerations of thermal stability and chemical resistance as were discussed in the case of crucibles (see p. 1775 ff.). The tube must be gas-tight. For this reason, it is usually closed at one end and carries a ground joint on the other (the latter is for evacuation and filling with inert gas); alternatively, it may carry high-vacuum valves or stopcocks on both ends (see Fig. 354). To protect the glass, quartz or ceramic tube *a* against corrosion by the volatile metal, a liner tube *b* (made of glass, ceramic material or metal such as Fe or Ni) may be inserted. Boat s_1 contains an excess of the volatile component, while boat s_2 is filled with the finest possible powder of the relatively nonvolatile reagent. Boat s_1 is also surrounded by a test-tubelike cylinder *c* which acts as a vapor deflector.

At the start of the run, a high vacuum is created in tube *a*. Then the two short, tubular electric heaters are switched on and regulated in such a way that a temperature sufficiently high to maintain a reasonable rate of distillation exists in s_1, while a slightly lower temperature exists in s_2. The temperature in s_2 should be sufficiently high to induce and maintain the reaction between the metal powder and the vapor arriving from s_1. At the end of the run, the excess of the volatile component is distilled off and condensed in the cooler section of the tube. Finally, the product is removed from boat s_2.

The above method is also useful for purifying a crude product obtained from two components by the crucible or ampoule fusion methods. The excess of the volatile component may thus be removed by vacuum distillation. In this case the vapor pressure of

the free volatile component must, of course, be much higher than its pressure in the residual intermetallic phase. Examples of application of this method are preparations of silicides and germanides of alkali metals, and of Na_3As and K_3Sb.

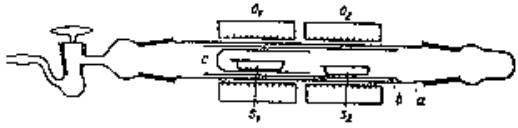

Fig. 354. Preparation of alloys by distillation. a reactor tube; b liner tube; c vapor deflecting cylinder; s_1, s_2 boats; o_1, o_2 tubular electric heaters.

The same principle can also be applied to the Faraday sealed-tube system described in Part I, p. 76 f. This system is completely closed and the only external influence consists of the temperature gradient; direct handling is not possible in this case. However, if the reactor tube material is resistant to corrosion by the reagents involved, the Faraday system produces an extremely pure reaction environment.

DropBooks

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Residue Methods

Occasionally, a pure component (α) phase may exhibit properties markedly different from those of the intermetallic phase which is vicinal to it on the constitutional diagram. Thus, the α-phase may dissolve more readily in a solvent or it may be attacked more readily by a reagent. In such cases it may be possible to use an excess of the pure component during the high-temperature synthesis and then liberate the intermetallic product by leaching out the matrix phase. Occasionally, also, slow cooling of the alloy melt may yield well-formed crystals of the intermetallic phase embedded in the pure component matrix, which may then be removed by some solvent. Depending on circumstances, the matrix phase may be removed by electrolytic oxidation, by aqueous acids, by bases, or by liquid NH_3. For example:

I. Electrolytic solution processes may be used to isolate semi-metallic compounds from the matrix in which they are produced:

Thus, for instance, Fe_3C may be isolated by electrolytic oxidation of the surrounding carbon-rich steel (see p. 1503). Other carbides such as $(Fe, Cr)_3C$, $(Cr, Fe)_7C_3$, $(Fe, Mn)_3C$, $(V, Fe)_4C_3$ and Fe_3Mo_3C are prepared in a similar manner. A procedure and an especially elegant apparatus have been developed by Klinger and Koch. This procedure has been employed primarily for the study of steels containing non-metallic admixtures, but should be usable for a more general study of alloys.

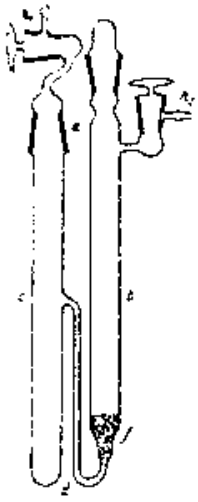

Fig. 355. Extraction of alkali metal alloys with liquid ammonia.

II. Aluminum compounds such as Al_3Ti, Al_3Zr, Al_3Th, Al_3V, Al_3Nb, Al_3Ta, Al_4Ce, Al_4La, AlB_2, etc., may be isolated from the Al-rich (matrix) products of the corresponding aluminothermic reactions, the solvents being dilute acids or bases. In a similar way, some silicides such as $ZrSi_2$, $ThSi_2$, VSi_2, $NbSi_2$, $TaSi_2$, $MoSi_2$, WSi_2 and USi_2 may be produced in molten aluminum "solvent" and then isolated as residues from treatment of the respective aluminum alloys with acids or bases (see p. 1794).

III. A special case is the isolation of intermetallic compounds of alkali or alkaline earth metals (except Be and Mg) by extraction with liquid ammonia. The alkali or alkaline earth metal, in considerable excess, is fused with the alloying component, the mixture is slowly cooled to obtain large crystals, and the solidified melt is then transferred without being exposed to air (the apparatus in Fig. 349 is quite appropriate here) into an extraction apparatus such as the one shown in Fig. 355. This device was developed on the basis of the arrangement of Biltz and Rahlfs (see Part I, Fig. 71). The alloy to be extracted is introduced through *a* and placed on top of the dense glass-wool filter *f*. The stopcocks h_1 and h_2 are both connected to a single vessel so that one can establish a high vacuum in the system, introduce NH_3 to one (or both) tubes, or establish a connection between tubes *b* and *c*. Some NH_3 is condensed in *b*, where it contacts the alloy on *f*; the blue solution of the alkali metal is then allowed to pass via the interconnecting tube *d* into tube *c*. There NH_3 is evaporated, leaving behind the free alkali metal. The NH_3 vapor is recycled to *b* for recondensation. Several repetitions of this operation allow exhaustive extraction of the alloy on *f*. The desired compound, which

is completely resistant to or attacked only slightly by the NH_3, remains as a residue on *f*.

The apparatus shown in Part I, Fig. 73 may also be used for the extraction of alloys with liquid ammonia.

The above method was used to produce Na_3As, Na_3Sb, Na_3Bi, $Na_{15}Pb_4$, $Na_{15}Sn_4$, $NaZn_{13}$ and Na_2Au. Pure, well formed single crystals were obtained.

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DropBooks

Special Processes

Intermetallic and metalloid compounds may also be prepared by methods other than those described in the preceding sections. However, these other processes have so far been used only in special cases, since the necessary conditions tend to limit their general applicability.

I. SIMULTANEOUS CHEMICAL REDUCTION OF NONMETALLIC COMPOUNDS AND ALLOYING OF NASCENT FREE METALS

For instance, reduction of niobium oxide and nickel mixtures by means of hydrogen leads to Ni-Nb alloys [1]. Thermal decomposition of isomorphous mixtures of Fe, Co or Ni formates or oxalates, conducted under reducing conditions, gives fine, crystalline alloy powders. These alloys correspond to phase equilibria at comparatively low temperatures [2].

II. SYNTHESIS OF BINARY ALLOYS AND INTERMETALLIC COMPOUNDS BY COMBINING SOLUTIONS OF BOTH COMPONENTS

The solvent may be a third, more or less inert metal, usually with a low melting point (Hg, Al or Mg). The process temperatures

thus range between ambient and several hundred degrees. For basic data on the precipitation of intermetallic compounds, see [3].

The Hg solution method may be used for the preparation of many intermetallic compounds, as well as very reactive metals. This is because the Hg solvent can be distilled off at a comparatively low temperature. The method can thus be used for preparation of alloys which cannot be obtained by fusing or sintering at high temperatures (see Amalgam Metallurgy [4]).

Aluminum compounds (silicides, borides, and so forth) can be prepared in liquid Al (see p. 1797 ff.). Special silicides may be obtained in liquid Cu (see p. 1796).

Liquid NH_3 may also be used as a solvent, especially in the synthesis of alloys of alkali and alkaline earth metals. However, this method has so far been used mostly for nonmetallic or metalloid alkali compounds [5].

III. ELECTROLYTIC DEPOSITION OF ALLOYS FROM AQUEOUS SOLUTIONS.

The composition of the alloy depends on the composition of the electrolyte, the reaction conditions, and special additives which favor the precipitation. Just as in the case of solidification of melts, alloys precipitated by the electrolytic method consist of heterogeneous crystallizates, solid solutions, or some intermediate phases. They may differ from the alloys produced at high temperatures. The differences may show up in phase boundaries and in some physical and engineering properties [6].

The following binary alloy systems have so far been prepared in this way: Cu-Zn, Cu-Sb, Cu-Bi, Cu-Pb, Ag-Zn, Ag-Cd, Ag-Au, Ag-Bi, Ag-Pb, Au-Cu, Au-Ni, Ni-Zn, Ni-Cd, Ni-Fe, Zn-Cd, Pb-Sn, W-Ni, W-Co and W-Fe.

Some intermetallic or metalloid compounds may also be obtained by high-temperature electrolysis of liquid melts of the corresponding metal compounds. Secondary reactions sometimes play an important role in this case. This method, developed mainly by Andrieux and Dodero [7], has so far been used for borides (see p. 1798), silicides (see p. 1796 f.), phosphides, arsenides and carbides.

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Silicides

A summary of processes for the preparation of metal silicides is given in Table 5.

I. MOISSAN'S CLASSICAL PROCESS (FUSION OF THE ELEMENTS)

These reactions are usually highly exothermic; the charge thus heats up far above its melting point, and a closely controlled reaction becomes impossible due to interaction with the walls of the vessel and gases, as well as volatilization of reagents; product purity and the yield are usually poor.

a) Silicides of transition metals, especially those of metals of Groups IV to VII, may be successfully prepared by sintering mixtures of powders of the constituents at comparatively low temperatures (< 1500°C). In this case, external heating must be discontinued promptly at the beginning of the exothermic reaction to avoid melting of the charge. The starting materials must be extremely pure and have a particle size < 0.06 mm. The powder mixtures are either tableted or pressed into alumina or graphite crucibles. They are heated in argon or in vacuum. Under these conditions, side reactions with the crucible materials are usually negligible.

Table 5

Preparation of Metal Silicides

Process	Reactions involved
I. Synthesis from the elements	
a) By fusion	$M + Si \rightarrow MSi$, $MH + Si \rightarrow MSi + H_2$
b) By sintering or sintering under pressure	
II. Reaction of metal oxides with Si or SiO_2 (silicates) and C	$MO + Si \rightarrow MSi + SiO$ $MO + SiO_2 + C \rightarrow MSi + CO$ M silicate + $C \rightarrow MSi + CO$ (unfavorable: $MO + Si \rightarrow MSi + SiO_2$, $MO + SiC \rightarrow MSi + CO$)
III. a) Aluminothermic and magnesothermic processes	$MO + Al(Mg) + SiO_2 + S \rightarrow$ MSi (in Al) + Al(Mg)–S-containing slags
b) Aluminum silicide process	$Al\text{–}Si + M \rightarrow MSi$ (in Al) $Al\text{–}Si + MF_2 \rightarrow MSi$ (in Al) + AlF_3 $Al\text{–}Si + MO + NaF \rightarrow$ MSi (in Al) + Na_3AlF_6 + Al_2O_3
c) Copper silicide process	$Cu\text{–}Si + M \rightarrow MSi$ (in Cu) $Cu\text{–}Si + MO \rightarrow MSi$ (in Cu) + $CuO \cdot SiO_2$
IV. Electrolysis of a melt	$K_2SiF_6 + MO \rightarrow MSi + KF$
V. Vapor-deposition process	$M + SiCl_4 + H_2 \rightarrow MSi + HCl$

b) According to Kieffer and Cerwenka, the density of the material can be increased even during the heating process, the result being a better product. A Tammann furnace (see Part I, p. 39) is used. The powder mixture is pressed into strong, 15-mm.-I.D. graphite molds and heated at 200 kg./cm.^{2} and 1100–1500°C. After cooling, the surfaces of the samples thus obtained are ground, yielding a material containing only 0.02–0.05% C.

II. REDUCTION OF METAL OXIDES WITH Si, SiC OR SiO_2 (SILICATES) IN THE PRESENCE OF CARBON

In general, this process requires very high temperatures and yields fused products from which it is difficult to isolate well-defined

silicides. For this reason, this method is largely of historical interest. However, a modern variant is of some importance. In this variant, very pure Si is added to the metal oxide in the stoichiometric ratio. If the stoichiometric ratio is maintained exactly, all of the oxygen from the metal oxide will be bound to the Si, which then volatilizes as SiO. This method, which requires a vacuum but only relatively modest temperatures, yields very pure silicides.

The above process is applicable in all those cases in which both the metal and its oxide (which is reduced) have low vapor pressures at the reaction temperature (this is true of transition metals of Groups III to VIII). For instance, the process yields pure rare earth silicides, which are otherwise difficult to obtain. In this case the optimum reaction pressure is approximately 0.1 mm.

III. ALUMINOTHERMIC OR MAGNESOTHERMIC PROCESSES

The general method was invented by Hönigschmidt. It starts from metal oxides and SiO_2 and gives pure products if the nascent silicide is embedded in an excess of the reducing metal (preferably Al). This is achieved by using an excess of SiO_2 and of the embedding Al in the reaction mixture. Of course, the embedding aluminum metal becomes alloyed to some extent with the Si and the other metal of the mixture. The object of the embedding process is to form an ingot or nugget which can be easily separated from the surrounding nonmetallic slag. This separation is facilitated by the addition of fluxes (CaF_2, cryolite or CaO) to the reaction mixture (Al_2S_3, which was used by Hönigschmidt, is not recommended). The silicide can then be isolated from the nugget by reaction with dilute acid or alkali. It is obtained in the form of a crystalline powder.

Some processes for silicides start from the metal itself rather than its oxide. The metal is thus reacted with Si in the presence of a melt of a third metal which serves as the solvent. Aluminum is usually the optimum solvent. Another method employs components initially prealloyed with Al (for instance, $ThSi_2$ is made from Th-Al and Si-Al alloys). Still another process proceeds by stages, whereby the components of the silicide are prepared *in situ* from other compounds, primarily a metal fluoride or oxide and an alkali fluoride. The nascent components then form the silicide.

In all the above variants of the basic process, the silicide is always embedded in excess Al. The process has been used for $NbSi_2$, $TaSi_2$, $ThSi_2$, $MoSi_2$ and WSi_2.

The Lebeau process, which uses copper as a solvent and an Si carrier, is no longer of any importance.

Alternate methods:

IV. ELECTROLYSIS

Silicides of Ti, Zr and Cr as well as those of the rare earth metals may be obtained by electrolysis of melts of the metals with silicates or fluorosilicates of suitable composition.

V. VAPOR DEPOSITION

Silicide layers may be obtained from H_2-$SiCl_4$ mixtures by deposition of an incandescent filament.

Procedures for the preparation of silicides are also found in other sections of this book (see Alkali Silicides p. 989 f., magnesium silicide p. 921 f., calcium silicide p. 946 f., silicides of Ti, Zr and Th, p. 1249 f.).

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Borides

Table 6 lists the most important processes for the preparation of borides, especially those of the transition metals.

Table 6

Preparation of Metal Borides

Process	Reactions involved
I. Synthesis from the elements	
a) Fusion	$M + B \rightarrow MB$, $MH + B \rightarrow MB + H_2$
b) Sintering or sintering under pressure	
II. Aluminothermic and magnesothermic processes	$MO + B_2O_3 + Al(Mg) \rightarrow$ MB + Al(Mg) oxide
III. Reduction of oxides with carbon	$MO + B_2O_3 + C \rightarrow MB + CO$
IV. Boron carbide process	$MO(M, MH) + B_4C(C, B_2O_3) \rightarrow$ MB + CO
V. Electrolysis of a melt	MO + alkali (alkaline earth) borate + alkali (alkaline earth) fluoride → MB + alkali (alkaline earth) borate-fluoride
VI. Vapor-deposition processes	M (M halide) + B halide + $H_2 \rightarrow$ MB + hydrogen halide

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I. Synthesis via fusion of the elements entails such high heats of formation that the reaction temperatures become very high. As a result, there is interaction with the material of the vessel and the product boride becomes contaminated. On the other hand, all borides may be prepared by sintering the appropriate metal with amorphous boron powder, which should be as pure as possible (commercial grades now available contain 97–99% B). The reaction mixtures should be heated in alumina crucibles (W or Mo crucibles or boats may also be used) in vacuum (an argon atmosphere is occasionally also used). The reaction, which is always exothermic, starts at temperatures of 700–1200°C; the highest temperature may lie above 2000°C. In some cases, sintering under pressure in carbon tubes (mentioned as a possible method of synthesis for silicides—see p. 1796) can be used.

II. Reduction with Al or Mg allows the use of oxides as starting materials and eliminates the preparation of pure boron. On the

other hand, this method involves inconvenience of chemical separation of the product boride crystals from by-products. This separation becomes especially difficult in the case of products of the aluminothermic preparation of high-melting borides (those of transition metals of Groups III to VI). No solid ingot or nugget is formed in this case; the fine boride powder is occluded in Al_2O_3 slag. According to Andrieux and Peffen, an excess of B_2O_3, CaO and Na_2O should be added to the reaction mixture. The alumina slag thus becomes soluble in acids and may be separated more easily from the boride powder.

III. Originally the preparation of borides of metals such as Ti and Zr from B_4C involved a reaction in hydrogen:

$$7\,Ti + 3\,B_4C + B_2O_3 = 7\,TiB_2 + 3\,CO$$

or

$$3\,Ti + 2\,B_4C + TiO_2 = 4\,TiB_2 + 2\,CO$$

Recently, however, a simpler process has been devised:

$$2\,TiO_2 + B_4C + 3\,C = 2\,TiB_2 + 4\,CO$$

The mixture of starting materials is pressed into pellets and heated in a tubular carbon furnace under high vacuum. Maximum temperatures of 1400-1900°C are required to produce the metal boride within a reasonable time. The method has been tested for borides of Ti, Zr, V, Nb, Ta and W.

Alternate methods:

IV. Small quantities of pure boron compounds can be prepared by electrolysis of melts. Boron, which is evolved on the cathode from alkali and alkaline earth borates, combines with the simultaneously precipitated metal.

V. Passage of gaseous mixtures consisting of a metal halide, BBr_3 and H_2 over incandescent carrier metals on the average yields only boride layers inhomogeneous, and solid products.

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Amalgams

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While some low-melting (< 1000 °C) metals fail to form alloys with mercury, the majority may be amalgamated simply by heating

Table 7

Solubility of Metals in Mercury at about 20 °C (after Jangg and Bach)

Metal	Solubility in weight %	Metal	Solubility in weight %	Metal	Solubility in weight %
Ag	0.03	In	57	Ru	0.35
Al	$2.3 \cdot 10^{-3}$	K	0.38	Sb	$2.9 \cdot 10^{-3}$
As	0.24	La	0.013	Si	$1 \cdot 10^{-3}$
Au	0.13	Li	0.036	Sn	0.87
Ba	0.33	Mg	0.81	Sr	1.0
Be	$1 \cdot 10^{-3}$	Mn	$1.7 \cdot 10^{-5}$	Ta	0.01
Bi	1.4	Mo	$< 2 \cdot 10^{-6}$	Th	0.016
Ca	0.3	Na	0.62	Ti	$1 \cdot 10^{-3}$
Cd	~ 5.0	Ni	$2 \cdot 10^{-6}$	U	$1 \cdot 10^{-3}$
Co	$< 1 \cdot 10^{-6}$	Pb	1.5	V	$1 \cdot 10^{-3}$
Cr	$< 4 \cdot 10^{-7}$	Pd	0.09	W	$1 \cdot 10^{-3}$
Cu	$2 \cdot 10^{-3}$	Pt	$2 \cdot 10^{-3}$	Zn	2.0
Fe	$< 5 \cdot 10^{-7}$	Rb	1.4	Zr	$3 \cdot 10^{-3}$
Ce	$1 \cdot 10^{-3}$	Rh	0.16		

with mercury in closed iron crucibles or glass ampoules. Under special circumstances, these vessels may also contain special insert crucibles (see p. 1774 ff.). This simple process applies to all permissible amalgam compositions.

Another general method for preparation of amalgams consists of the electrolysis of solutions of the respective metal salts in cells comprising an Hg cathode. The concentrations of the respective metals in the amalgam reach very high levels so that solid phases may separate. The method is applicable even to metals with extremely low solubility in Hg (for example, Fe); in this case, the method gives suspensions of the metal in Hg which exhibit behavior very similar to that of "true" amalgams (see Table 7).

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It is sometimes desired to prepare liquid or semisolid amalgams of base metals for special purposes, especially for use as laboratory reducing agents. The following simple methods apply in these cases:

SODIUM AMALGAM (LIQUID; ABOUT 1% Na)

I. Clean sodium metal (11.5 g.) is cut into 5-mm. cubes. The cubes are speared with a pointed glass rod and rapidly introduced below the surface of warm (30-40°C) pure mercury (1150 g. = 85 ml.) contained in a 500-ml. wide-neck Erlenmeyer flask. The flask is covered with cardboard to prevent spattering during the rather vigorous amalgam formation reaction.

II. In another method, 3.5 g. of Na protected by a layer of toluene (10-15 ml.) is melted in a 250-ml. Erlenmeyer flask placed on a hot plate. Then, 340 g. (25 ml.) of Hg is added in drops (stirring or shaking). The first few drops of mercury cause a vigorous reaction, but then the amalgam formation becomes less violent. The toluene boils during the entire addition; at the end, it is decanted or displaced with other liquids.

The following method for solid amalgams may be modified and adapted to other ratios of reagents.

SODIUM AMALGAM (SOLID; ABOUT 2-3% Na)

I. The Fieser procedure gives especially pure material: Clean sodium pieces (6.9 g. for an amalgam containing 2% Na, 10 g. for one containing 3% Na) are placed in a 250-ml. three-neck

round-bottom flask. The two side necks carry nitrogen inlet and outlet tubes, while the center neck carries a dropping funnel containing 340 g. (25 ml.) of Hg. The flask is thoroughly flushed with N_2, and 10 ml. of Hg is then added. The flask is heated on an open flame until the start of the reaction. Additional Hg is then slowly added, with minimum additional heating. After the addition, the hot molten amalgam is poured onto a clean plate and broken up into pieces while still hot and brittle.

II. Another method is useful for preparation of larger quantities of amalgam. Thus, for example, 51 g. of clean, freshly cut sodium is heated in an enameled pot (about 18 cm. I.D.) under paraffin oil until molten (the thickness of the protective oil layer should be 1 cm.). Then, 1650 g. (122 ml.) of Hg is added slowly (constant stirring) from a dropping funnel. This reaction ends within 3-4 minutes, and most of the paraffin is decanted. The amalgam solidifies at about 250°C. During cooling, it is comminuted with a heavy pestle to form small beads. Alternatively, the hot liquid amalgam may be poured (together with the adhering oil) into a porcelain dish and allowed to solidify; the cake is then broken up to the desired particle size in a mortar. After complete cooling the oil is removed by washing with petroleum ether or benzene. The solvent is then evaporated, and the product stored in an air-free atmosphere.

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PROPERTIES:

Amalgams containing less than 3% Na are not too sensitive to air; however they must be stored in an air-free atmosphere. Complete liquefaction occurs at the following (liquidus) temperatures: 0.5% Na, 0°C; 1.0% Na, 50°C; 1.5% Na, 100°C; 2.0% Na, 130°C; 2.5% Na, 156°C; 3% Na, 250°C; 4.0% Na, 320°C.

REFERENCES:

Organic Syntheses, Collective Volume 1, New York-London, 1941, p. 539; W. R. Renfrow, Jr., and C. R. Hauser in: Organic Syntheses, Collective Volume 2, New York-London, 1950, p. 609; V. Deulofeu and T. H. Guerrero in: Organic Syntheses, Vol. 22, New York-London, 1947, p. 92; S. H. Babcock in: H. S. Booth. Inorganic Syntheses, Vol. 1, New York-London, 1939, p. 10; L. F. Fieser. Experiments in Organic Chemistry, New York, 1941, p. 419.

POTASSIUM AMALGAM

For preparation, see A. Roeder and W. Morawietz, Z. Elektrochem. 60, 431 (1956).

CALCIUM AMALGAM

The reactor is a small steel bomb *b* (Fig. 356). The vertical part of the top opening carries a flat thread into which is screwed the steel head *k*. While the two parts should fit each other well, one should be to unscrew *k* without too much difficulty. The conical extended surface above the thread provides additional sealing area. The seal should hold at better than 70 atm. The head *k* carries a pressure-reducing valve *r* connected to pressure gage *m* and pressure tubing *d*, which leads to a compressed nitrogen cylinder. A piston *s*, located inside the bomb and actuated by the gas from the cylinder, fits the walls fairly tightly.

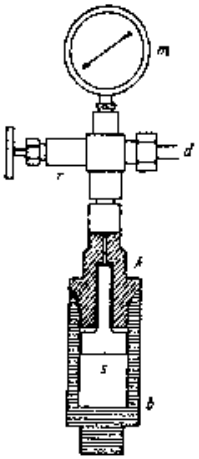

Fig. 356. Preparation of calcium amalgam. *b* steel bomb, 19 cm. long, 5.5 cm. I.D., 9 mm. wall thickness; capacity 45 ml. up to the screw thread; *s* movable piston; *k* steel head; *r* pressure-reducing valve; *m* pressure gage; *d* copper preassure tubing for introduction of N_2.

To start with, the bomb is charged with 35 ml. of pure Hg. Then, 7–10 g. of shavings of commercial Ca are added and the piston set in place. The bomb is tightly closed and nitrogen injected to a pressure of 60–70 atm. above the piston. The formation of the amalgam starts immediately, heat of reaction is evolved, and the bottom of the bomb becomes hot; the reaction ends in no more than 10–15 minutes. The pressure is released and the bomb is opened. The amalgam is rapidly transferred to a dry, wide-neck flask of about 60-ml. capacity, which is then tightly closed. The steel bomb is rinsed with some pure Hg. This material is added to the flask, which is then filled with Hg to just below the stopper (the amalgam in the flask heats up considerably on dilution with the Hg). The mixture is shaken well and allowed to cool.

PROPERTIES:

This amalgam contains about 1% Ca; sometimes solidifies in the cold; can be stored indefinitely in containers completely filled with mercury. According to data in M. Hansen and K. Anderko, Constitution of Binary Alloys, the liquidus curve in the Ca-Hg system rises to about 260°C at 2% Ca, 140°C at 1% Ca, and 25°C at 0.3% Ca; most of this amalgam solidifies at the peritectic point of −39°C.

REFERENCE:

A. Brukl. Angew. Chem. 52, 151 (1939).

STRONTIUM AND BARIUM AMALGAMS

Strontium and barium amalgams are prepared by electrolysis of solutions of the corresponding chlorides on mercury cathodes. The directions for the compound are each applicable to the other.

STRONTIUM AMALGAM

The cell *a* of the apparatus shown in Fig. 357 contains about 300 ml. of a saturated solution of pure $SrCl_2$, made weakly acidic with HCl (if contaminated with traces of Na and Fe the salt must be prepurified). The cathode *b* consists of 600 g. (45 ml.) of pure, distilled Hg. The thick Pt wire *c*, which dips into the mercury pool, is the current lead. The anode is a graphite rod *e* (10 mm. O.D.) suspended in a porous clay cell *d* which dips into the liquid. The electrolysis proceeds at a current of 6.5 amp. (that is, at 1.7 amp./in.^{2}, considering the 24 cm.^{2} of cathode surface). The passage of the current causes a sharp temperature rise and the electrolyte is maintained at the optimum temperature of 38–40°C by means of cooling coils *g* and *f* wound on the outer surface of cell *a* and immersed in the solution. The liquid in the anode space is replaced every 15 minutes to prevent accumulation of Cl_2 and its penetration into the cathode space. The Sr content in the Hg reaches 1.3% in 90 minutes; at this point the amalgam becomes a slurry because the liquidus point for this composition is reached. The current is shut off and the electrolyte is poured out from the cell. The amalgam is then removed, washed several times with water, and dried with filter paper.

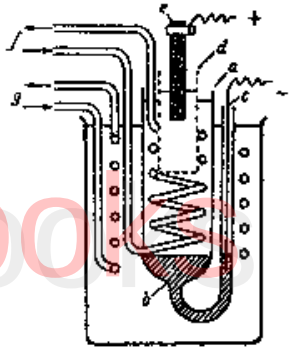

Fig. 357. Preparation of strontium amalgam. *a* electrolysis cell; *b* mercury cathode; *c* current lead (Pt wire); *d* porous clay cell; *e* anode (graphite rod); *f*, *g* water-cooled coils.

PROPERTIES:

Silvery, shiny, solid at room temperature. Must be stored in air-free atmosphere.

REFERENCE:

L. Holleck and W. Noddack, Angew. Chem. 50, 819 (1937).

BARIUM AMALGAM (APPLICABLE ALSO TO STRONTIUM AMALGAM)

The cell consists of a 250-ml. beaker. The cathode is a pool of 250 g. (18 ml.) of pure mercury. A Pt wire, all of it except for the tip sealed in glass to prevent contact with the electrolyte, dips into the mercury pool and serves as the current lead. The anode is a horizontal sheet of Pt, 5-10 $cm.^2$ in area.

The cell is filled with 100 ml. of saturated $BaCl_2$ solution. The electrolysis proceeds at a current of 1.75-2.5 amp. and 6-7 v. The current should be shut off after 2.5 hours, since beyond that time there occurs a sharp voltage rise, evolution of gas at the cathode and decomposition of the amalgam. Sometimes, crystalline amalgam particles deposit on the mercury surface and interfere with the electrolysis. This deposition may be prevented by slow agitation with a stirrer, or the crystals may be pushed into the body of the mercury with a glass rod.

At the end of the run the solution is decanted and the amalgam is thoroughly washed with distilled water, followed by ethanol and ether. It contains about 3% Ba. Is is stored in an air-free atmosphere.

REFERENCES:

G. McPhail Smith and A. C. Bennett, J. Amer. Chem. Soc. 31, 804 (1909); B. C. Marklein, D. H. West and L. F. Audrieth in: H. S. Booth, Inorg. Syntheses, Vol. 1, New York-London, 1939, p. 11.

ZINC, CADMIUM, TIN, LEAD AND BISMUTH AMALGAMS (LIQUID)

The liquid zinc amalgam (2-3% Zn) is prepared from 4 g. of zinc (granules, shavings; preferably, however, foil). The zinc is degreased with ether, thoroughly washed with dilute H_2SO_4, placed in a 100 ml. flask, and heated on a water bath together with 200 g. (14.8 ml.) of Hg and 2 ml. of 1N H_2SO_4. The Zn dissolves completely in about 20 minutes. The liquid amalgam is repeatedly washed with very dilute H_2SO_4, cooled and separated in a dropping funnel from solid particles (β or γ phase, composition approx. $HgZn_2$). These solids may be used to enhance the Zn concentration of amalgams that have lost some Zn during use. The liquid Cd and Bi amalgams (each containing about 3% of the respective metal)

are prepared in an analogous fashion. However, the Bi amalgam is prepared with hydrochloric rather than sulfuric acid. The Sn amalgam (8% Sn) is prepared by heating Sn granules with Hg under hydrochloric acid. The liquid Pb amalgam (3% Pb) by heating dry Pb with the stoichiometric quantity of Hg (the starting Pb must be freed of surface oxide by treatment with conc. HCl). The amalgam product is washed with water.

PROPERTIES:

The above liquid amalgams are very stable and may be stored for a long time under weakly acidic water, with which they react extremely slowly.

Used as reducing agents in volumetric analyses.

REFERENCES:

E. Brennecke. Flüssige Amalgame als Reduktionsmittel in der Massanalyse [Liquid Amalgams as Reducing Agents in Volumetric Analysis], in: Brennecke, Fajans, Furmann, Lang and Stamm. Neuere Massanalytische Methoden [New Methods of Volumetric Analysis], Stuttgart, 1951; also contains references to original publications. C. Winterstein, Z. anal. Chem. 117, 81 (1939).

DropBooks

AMALGAMS OF RARE EARTH METALS

Amalgams of rare earth metals (3% of the metal) are readily obtained by electrolysis of alcoholic solutions of the corresponding anhydrous chlorides at an Hg cathode and a graphite anode. These amalgams may be then further concentrated by distilling off the excess Hg.

REFERENCES:

E. E. Jukkola, L. F. Audrieth and B. S. Hopkins in: H. S. Booth, Inorg. Syntheses, Vol. 1, New York-London, 1939, p. 15.

ALUMINUM AMALGAM

The normal procedure is to deposit only a surface layer of amalgam on the metal, in order to activate it for use in some specific reaction [H. Adkins, J. Amer. Chem. Soc. 44, 2175 (1922)].

Potassium-Sodium Alloy (liquid)

The constitutional diagram of the K-Na system shows a liquidus curve minimum at −12.5°C corresponding to 77.3 wt. % K. All alloys with compositions near this point (45-90 wt. % K) are liquids at room temperature and are much more reactive than the pure metals.

Alloys such as these are prepared by carefully heating, for instance, 3 g. of clean pieces of K and 1 g. of clean pieces of Na (or other required quantities of these metals) under anhydrous toluene or xylene, while kneading the two metals with a flat-end glass rod.

According to Lecher, the metals may be combined even at room temperature provided some ethanol is added to the protective fluid in order to activate the metal surface. The vessel is a Schlenk flask, which consists of a two-neck glass bulb (one of these necks is narrow and vertically centered, the other is inclined and somewhat to the side of the flask). An alloy useful in organic reactions may be obtained from 0.35 g. of Na and 1.6 g. of K, which are combined under weakly alcoholic ligroin while a stream of nitrogen is introduced via the side neck (the metals are kneaded by means of a flat-end glass rod introduced through the vertical neck). After a liquid alloy has been obtained, the nitrogen purge is continued while the alcoholic ligroin (including the impurities suspended in it) is replaced by clean, anhydrous ligroin.

The Schlenk flask may, of course, be replaced by other devices which allow work in the absence of air. The liquid alloy ignites spontaneously and must always be protected by an inert fluid and an inert gas (N_2, CO_2).

REFERENCES:

H. Lecher, Ber. dtsch. chem. Ges. 48, 524 (1915). For constitutional diagrams and crystal structures of the K-Na and other binary systems of alkali metals, see also A. Helms and W. Klemm, Z. anorg. allg. Chem. 242, 201 (1939).

Low-Melting Alloys

Low-melting alloys are often required for special purposes such as for heating baths or manometers, sealing in other liquids or gases, cementing, and for flowout devices. Some of these alloys, all of which are reasonably stable in air ar their melting points and somewhat above, are listed below.

Designation	M.p., °C	Composition, wt. %
Bi-Cd-Pb-Sn eutectic (Wood's Lipowitz metal)	71	49.5 Bi/10.1 Cd/27.3 Pb/13.1 Sn
Bi-Cd-Pd eutectic	91.5	51.7 Bi/8.1 Cd/40.2 Pb
Bi-Pb-Sn eutectic (Newton's Rose metal)	96	50 Bi/31.2 Pb/18.8 Sn
Bi-Cd-Sn eutectic	103	54 Bi/20 Cd/26 Sn
Bi-Pb eutectic	125	56.5 Bi/43.5 Pb
Bi-Sn eutectic	139	58 Bi/42 Sn
Cd-Pb-Sn eutectic	145	18.2 Cd/32 Pb/49.8 Sn
Pb-Sn eutectic	183	37.7 Pb/62.3 Sn
Sn-Zn eutectic	198.6	91.1 Sn/8.9 Zn
Cd-Zn eutectic	266	82.6 Cd/17.4 Zn
Ag-Pb eutectic	304	2.5 Ag/97.5 Pb

Further special alloys can be obtained with Ga and In:

Designation	M.p., °C	Composition, wt. %
Ga-In-Sn-Zn eutectic	3	61 Ga/25 In/13 Sn/1 Zn
Ga-In-Sn eutectic	5	62 Ga/25 In/13 Sn
Ga-In-Zn eutectic	13	67 Ga/29 In/4 Zn
Ga-In eutectic	16	76 Ga/24 In
Ga-Sn eutectic	20	92 Ga/8 Sn
Ga-Zn eutectic	25	95 Ga/5 Zn
L 46	46.5	40.6 Bi/8.2 Cd/18 In/22.4 Pb/10.8 Sn
L 58	58	49 Bi/21 In/18 Pb/12 Sn
In-Sn eutectic	117	52 In/48 Sn

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An exhaustive review of alloys melting between −39°C and +419°C is given by Spengler. If the low-melting alloys are used as cements or solders for nonmetallic objects, or if they are melted in nonmetallic vessels, then the thermal expansion coefficients must be carefully considered. For instance, Wood's metal may, on cooling and resolidification, burst glass vessels in which it is contained for use as a bath liquid.

REFERENCES:

H. Spengler, Metall 9, 682 (1955); Z. Metallkunde 46, 464 (1955); J. D'Ans and E. Lax, Taschenbuch f. Chemiker and Physiker

[Handbook for Chemists and Physicists], Berlin-Göttingen-Heidelberg, 1959; M. Hansen and K. Anderko. Constitution of Binary Alloys, New York-Toronto-London, 1958; C. J. S. Smithells. Metals Reference Book, London, 1949; M. T. Ludwick (The Indium Corp. of Amer.), Indium etc., New York, 1950; W. Kroll. Metallwirtschaft 11, 435 (1932).

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NOTE: Rare earth elements (lanthanides) are designated by the common symbol Ln (except in special cases where R.E. has been used). Thus, for their compounds see under Ln.

A

Ag 1029, 279, 1028
Ag_2C_2 1047
$Ag(CF_3COO)$ 205
$Ag_2C_4H_4O_6$ 1049
$AgCN$ 661
Ag_2CN_2 1047
Ag_2CO_3 1048
$AgClO_3$ 1037
$[Ag(dipyr)_3](ClO_4)_2$ 1050
$[Ag(dipyr)_2]NO_3$ 1050
$[Ag(dipyr)_3](NO_3)_2$ 1051
$[Ag(dipyr)_2]S_2O_8$ 1051
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AgI 1035
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$Al(C_2H_5)_3$ 810
$Al(C_2H_5)_2Br$ 809
$Al(CH_3COO)_3$ 835
$Al(C_2H_5)_2Cl{\cdot}O(C_2H_5)_2$ 811
$Al(C_2H_5)_2H$ 811
$Al(C_5H_7O_2)_3$ 836
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$Al(OC_2H_4)_3N$ 835
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$Al_2O_3{\cdot}3SO_2{\cdot}xH_2O$ 824
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$B(C_2H_5)_3$ 799
$B(C_nH_{2n+1})_3$ 800
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$BF_3 \cdot 2H_2O$ 784
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$[Cr(OH_2)_6]Cl_3$ 1348
$[Cr(OH)_6]Na_3$ 1688
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505	1	. . . a drop of KI-starch solution, i.e., whether the desired large excess of nitrite is present. If this is not the case, one must either wait a while or add some more nitrite. Then 25 ml. of 10N . . .

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